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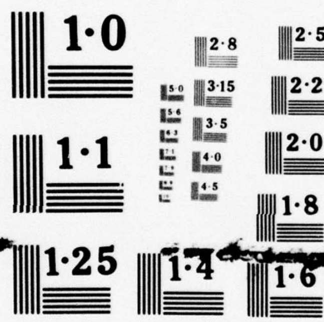

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RARE EARTH CERAMIC TECHNOLOGY (U.S.S.R.)

MORTON I. KLIMAN
CERAMICS RESEARCH DIVISION

January 1978

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ABSTRACT

This study presents and documents an analysis of the sources and uses of rare earth element oxides and ceramics in the Union of Soviet Socialist Republics. The purpose of this study is to provide an adequate basis for the comprehension of the strategic background for the uses of rare earth compounds. With this knowledge the addition of new information can be properly applied to understand the level of technology and rate of advancement of rare earth compound technology within the U.S.S.R. as well as other nations. This data base is intended to provide further support for the acquisition and placement of new data into proper perspective for rapid, up-to-data technological assessments. The information contained in this study is based upon open source scientific and technical literature.

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CONTENTS

PREFACE

This study presents and documents an analysis of the sources and uses of rare earth element oxides and ceramics in the Union of Soviet Socialist Republics. The rare earth elements and their compounds are found in a wide variety of both raw and sophisticated industrial and strategic uses. Many of the modern applications of rare earth compounds did not exist ten years ago, and the major applications of the next decade are far from commercialization at the present time.

The purpose of this study is to provide an adequate basis for the comprehension of the strategic background for the uses of rare earth compounds. With this knowledge the addition of new information can be properly applied to understand the level of technology and rate of advancement of rare earth compound technology within the U.S.S.R. as well as other nations. This data base is intended to provide further support for the acquisition and placement of new data into proper perspective for rapid up-to-date technological assessments. It will also assist intelligence collectors and analysts in the performance of their assignments.

This study will supply the names, institutional affiliations and fields of expertise of scientific personalities of importance in Soviet rare earth activities. The identification of the chief institutes, their interrelated activities in rare earth research and development studies as well as the cooperative involvement of key personalities in their respective fields of interest will provide an important insight into target areas for the intelligence community to continuously monitor so as to reveal and identify advanced trends of potential military significance.

The information used to compile this study was taken from scientific and technical publications, Chemical Abstracts, Engineering Abstracts, Abstracts of the Journal of the American Ceramic Society, CIRC data base, and other sources. The pertinent references are listed at the end of each section for easy access to the reader and to permit sections of the report to be separated as a whole for independent analysis and usage.

The information contained in this study is based upon open source scientific and technical literature.

This study was sponsored by the U.S. Army Foregin Science and Technology Center, U.S. Army Materiel Development and Readiness Command, with Mr. Charles Petschke as the technical monitor.

EXECUTIVE SUMMARY

The rare earth elements comprise a grouping of chemical elements beginning with element atomic number 58 and ending with element atomic number 71. Due to the unsaturated nature of the inner atomic electron shells and the various quantum electronic energy levels possible, the rare earth elemental compounds and compositions possess and/or furnish properties specific to themselves only and not obtainable elsewhere. In many applications the rare earth elements are indispensable. The industrial and military usage of the rare earth elements in the form of ceramic compounds and compositions is important from a military strategic viewpoint because a knowledge of the amount of and sophistication of the applications of the rare earths yields valuable information relative to the trends in advanced military weaponry and its production support base. A knowledge of the state of the activity of rare earth ceramic usage is important for sound military strategic intelligence collection, review, and analysis.

The use of rare earth elements as neodymium and dysprosium in glass and inorganic crystalline hosts has been investigated by Soviet research workers for many years, resulting in a capability for design, formulation, and preparation of rare earth ions in structurally clean inorganic glasses and single crystals. The chief centers of this work are the P.N. Lebedev Physics Institute and the Shubnikoff Institute of Crystallography in Moscow. Slow but steady progress in rare earth ion-activated laser systems is to be expected with real military applications (as range finders) some years away; and laser weaponry applications are at least five to ten years off.

Soviet research and development workers have been active in the field of magnetohydrodynamic (MHD) powder generation for many years. They have achieved significant advances in their MHD generator operation using rare earth (Y_2O_3) stabilized zirconia refractories and lanthanum chromite channels and electrodes. These generators are capable of sustained operation at reduced temperatures. Although the materials problems are still not solved, the Soviet effort is well advanced over that of the United States effort. There is little likelihood the MHD powder generators will see early industrial or military use except for single-short high power applications. The primary focus of MHD research, development, and design activities is in Moscow at the Institute of High Temperatures and the Moscow Power Institute.

The Soviet effort on the use of yttrium aluminum garnet (YAG) either as a host for laser use, for electronic circuitry, or as a computer component is a strong, well-developed activity. The collaborative efforts of scientists and engineers at the P.N. Lebedev Physics Institute and the Shubnikoff Institute of Crystallography have resulted in the development of directional gradient crystallization, optical zone melting, and skull melting crystal production processes in addition to the conventional Czochralski method of crystal growth for producing high quality YAG; with the primary emphasis placed upon Nd^{3+} doped YAG for laser use purposes.

Yttrium iron garnet (YIG) is an essential component of radar, microwave communications systems, and electronic computer circuitry. The Soviet effort to form YIG of very sophisticated microstructural and electronic properties is noteworthy. The research effort is almost as advanced as the United States

effort. However, only limited and necessary use of YIG components in Soviet military hardware is evident. Industrial use is nonexistent. The application of YIG to electronic computer circuitry is not to be expected for at least a decade. Current usage of YIG in Soviet radar systems is well known.

The required emphasis on refractories for metallurgical use in the Soviet Union has resulted in the use of yttrium oxide to structurally stabilize zirconium oxide refractories. These specialized refractories are used in MHD power generators and chemical plants. The problem of destructive phase transformations resulting in the undesirable structural deterioration of refractory structures has been addressed by Soviet research personnel and has resulted in many papers and several patents. The use of yttrium oxide to stabilize zirconium oxide is different from United States practice which has depended upon calcium oxide for the crystal structure stabilization purpose. The Institute of High Temperatures in Moscow has developed the control of yttrium oxide-stabilized zirconium oxide to a high degree of refinement. The most noteworthy recent effort of the Institute of High Temperatures is the development of yttria-stabilized zirconia microspheres as a high-temperature-resistant filler material for refractory structures and for potential use as a heat storage material for high-temperature wind tunnels.

The primary use of rare earth compounds in the Soviet glass industry has been for special colorants for glass. The Gusev Crystal Glass Factory developed the use of rare earth oxides and other combinations to form attractive colored glass items for domestic and export purposes. There is no evidence to indicate the manufacture of photochromic glass in the Soviet Union. Special rare earth pigment combinations have been developed for glazes for procelains and earthenware pottery. These uses were well known in the United States some decades ago.

The massive use by Western Nations of rare earth zeolite catalysts for cracking petroleum to gain much higher yields of critical fuels has not been matched by the Soviet Union. In fact the research and development effort on these materials began only a few years ago and has at best advanced to a very preliminary pilot-plant stage. Although the Soviet Union possesses adequate rare earth material resources, there has been no effort to construct a plant to manufacture these specialized rare earth zeolite catalyst materials. The result is a lesser yield of the more useful products of the petroleum-cracking process from crude oil. The Soviet effort is at least 12 years behind that of the United States.

Although the number of non-oxide rare earth compounds is large, there has been only limited use made of them. The substantial interest in these compounds in the late 1950's and early 1960's rapidly diminished, except for some limited usage as electrode materials, when Dr. G.V. Samsonov turned his attention elsewhere as the expected uses did not develop.

There is an important body of work being performed in the Soviet Union on rare earth-containing electric/electronic materials. The activity is widespread and ranges from zirconia heating elements, to temperature-compensated capacitors, resistors, thick-film circuit pastes, thin-film electronic circuit elements, and electronic computer circuitry. However, the quality and scope of this work is far less than that of the Western Nations, whose emphasis on consumer and industrial electronics has left the Soviet Union from two to ten years behind Western technology.

I. GENERAL BACKGROUND

To form an appreciation of what the rare earth elements and their compounds are, it is important to realize the position of the lanthanides in the periodic system and their electronic structure. The lanthanide group, see Figure 1, comprises 14 elements with atomic numbers ranging from 58 (cerium) to 71 (lutecium). These elements are located in row six of the Periodic Table of the Elements following lanthanum, and their properties resemble lanthanum. For this reason lanthanum is usually included in this specialized group and the elements are called lanthanides; i.e., resembling lanthanum. In addition, scandium, atomic number 21, and yttrium, atomic number 39, which belong to Group III of the Periodic Table of the Elements, are chemical analogs of lanthanum, and because scandium and especially yttrium are almost always present together with the lanthanides in mineral configurations, they are also considered and treated as lanthanides.

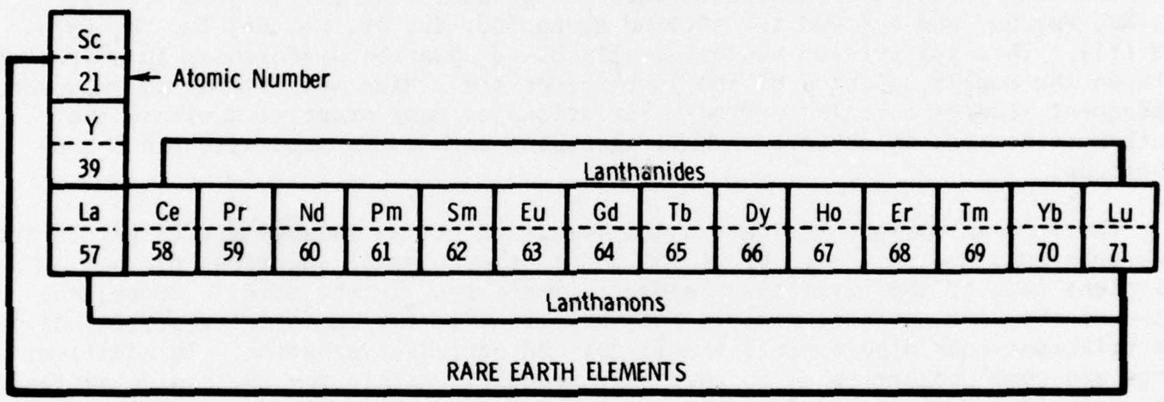


Figure 1. The rare earth elements

The lanthanides are usually placed separately in the Periodic Table of the Elements, often at the bottom of the table. They all possess very similar physicochemical properties due to the peculiar structure of their electron shells. It is well known that the chemical and most physical properties of the elements primarily depend upon the structure of the external electron shells. For the lanthanides the structure of the two outermost shells (the O and P shells) remains the same as the charge on the nucleus (i.e., the atomic number) is increased, because the transition from one element to another is attributable to the filling of the inner 4f electron level. The maximum number of electrons in the f orbital is 14, and this is also the total number of lanthanides. The 4f electrons are relatively unaffected by external factors because they are shielded by the electrons in the outer orbitals. Therefore, the 4f electron state exhibits almost no effect upon the chemical properties of the lanthanides.

In the basic ground state the lanthanide atoms (except gadolinium and lutecium) have no electrons in the 5d orbital. However, the transfer of an electron from the 4f to the 5d orbital requires only a small amount of energy. The valence of 3+ which is characteristic of the lanthanides is associated with the transfer of one electron from the 4f to the 5d orbital. The valence bonds

therefore involve two electrons from the outer 6s orbital and one electron from the 5d orbital. Furthermore, some lanthanides may exhibit a valence of 2+ or 4+ in addition to the 3+ valence state. These unusual or abnormal valence states are attributed to the variation in the ultimate binding strengths of 4f electrons with the number of electrons in that orbital state. The bond strength increases as the number of 4f electrons varies from 1 to 7 and again from 8 to 14. The maximum bond strength increases correspond to a half-filled and a completely filled 4f orbital. Therefore, gadolinium and lutecium possess the most stable f orbital configurations. A 4+ valence is exhibited by cerium and praseodymium (the first f electrons are easily transferred to the 5d orbital) and terbium and dysprosium which follow gadolinium in the series. A valence of 2+ is shown by samarium, europium, and ytterbium, i.e., as elements in which the number of electrons in the f orbital is either equal or close to seven.

The lanthanides are subdivided into two groups: the cerium group [(La), Ce, Pr, Nd, Pm, Sm, and Eu] and the yttrium group [Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu, and (Y)]. This subdivision was originally based upon the differences in solubility between the double sulfates of the lanthanides and sodium and potassium. However, subsequent studies revealed periodic variations of many properties within the lanthanide series, which were in full agreement with their separation into two subgroups.

There is an obvious analogy in the variation of the valency states within the two subgroups and in the color of the ions: the color of solutions of the trivalent ions of the first seven elements resembles, in the reverse order, the color of the next seven elements. The variations in the magnetic properties of the trivalent ions also exhibit a well-defined periodic variation. In addition, there are some properties which vary only gradually within the lanthanide series. The atomic and ionic radii decrease continuously as the atomic number is increased. This phenomenon, known as the "lanthanide contraction," is attributed to the slow decrease in the basic character of these elements in the transition from cerium to lutecium and is the cause of the different solubilities of the lanthanides and the chemical stability of their complex compounds.

In the past century the status of the rare earth elements and compounds has been transformed from a mere chemist's curiosity to a position of high esteem. This has been accomplished through their usage in some of the most intellectually and pragmatically sophisticated devices known to man. In essence, there is hardly a person in the advanced nations of the earth who has not seen, used, or in some way been affected by a particular application of the rare earth elements and their compounds. From delicately colored glazes for ceramic items to optically polished lenses for eyeglasses to special optical filters, through glass decolorizers, to fiber optic devices, to microwave filters, to low-temperature fracture-resistant steels for arctic petroleum pipelines, to laser devices and even non-impact print-out media for high-speed computers, the rare earth elements supply a critical difference in properties necessary for functional performance. It may well be concluded that the level of industrial and military sophistication of a nation is directly proportional to, or at the very least highly correlatable with, its knowledge of and usage of rare earth compounds. These uses number in the hundreds with requirements ranging from minute quantities as additions to major products as in the decolorizing of glass to tonnage quantities for polishing optical glass compounds. In fact, due to the specialized nature of the atomic structure of the

rare earth elements, which gives rise to specific interactions both alone and in combinations with other elemental structures (especially in the electronic field of endeavor), it is predictable that the number of uses of these elements will continue to expand at a high rate with new and unusual applications made of the rare earth elements in combinations with other materials which are now unforeseen, but which will be of great industrial and societal benefit.

II. UTILIZATION OF RARE EARTH COMPOUNDS IN LASER SYSTEMS (SOVIET)

1. Background

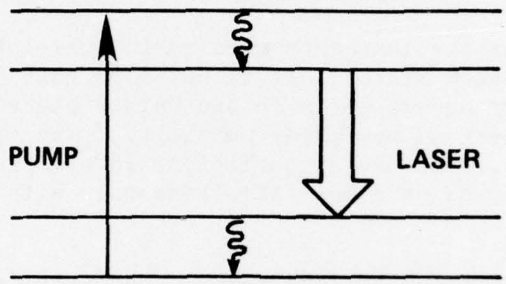
The rare earth ionic species has figured prominently in laser research development and technology from the very conceptual beginning of this important area. The atomic/electronic structure of the rare earth elements makes them particularly suited for use as atomic constituents of lasers. It is of interest to note the singular United States origin of the idea of lasers and that Schawlow and Townes[1] indicated in the disclosure section of their patent that europium and samarium as well as other rare earth elements were suitable for laser action. The multiplicity of electron quantum level transitions possible as well as the incompleted inner electron shells of the rare earths are responsible for their great utility in making up materials of interest in laser system design and application. The rare earth elements possess specific emission and fluorescence spectra in active media which cannot be duplicated by other elements.

The introduction of the lanthanon rare earth ions into laser technology began in 1961 in the United States. It is believed that Soviet physicists were aware of the early laser developments in the United States due to information in the scientific literature and newspaper publicity. The capabilities of Soviet mathematicians and physicists was of sufficient intellectual quality for theoretical analysis to be carried on almost simultaneously with the onset of the revealed conception.

The laser is, in fact, an optical maser. The turn 'maser' is an acronym derived from the first letters of the words "microwave amplification by stimulated emission of radiation." The "m" was origninally applied to devices used at microwave frequencies. With the extension of the frequency range through the use of similar principles it has been suggested that the word "molecular" be substituted for "microwave" as an all-inclusive generic term. In practice the term maser has been transformed into 'laser' through both popular and scientific use and custom. The word laser is now applied to all atomic amplifiers and generators without reference to wavelength ranging from far infrared frequencies to optical light waves and well beyond the ultraviolet into the X-ray frequency spectrum. The words laser and maser are now synonymous with the 'l' standing for "light." Laser now well accepted and used as such in the English and Russian Literature.

Laser action is a special form of luminescence. The primary requirement of a laser material is that it must emit radiation at a monochromatic wavelength when stimulated by optical, radio frequency, electrical, or other kinds of energy. The chief mode of laser action is to use an energy source imput to raise the electron quantum levels of atoms up to a particular excited state which, when a certain threshold level is reached, produces an electronic level saturation which results in a combined overall instantaneous drop to a lower quantum energy level giving rise to a rapid, simultaneous radiant energy emission at a wavelength characteristic of the specific ionic species. The rare earth elements therefore give rise to individually identifiable emission spectra permitting under appropriate conditions a selection of the specific wavelength of emitted radiation. The characteristics of close monochromaticity and a very sharply defined emissive field are very important and valuable distinguishing features of laser action.

There is an important requirement for a laser host material for the specific rare earth ionic species which can be activated by an energy source to perform the appropriate sequence of events. For efficient, high-power, accurate responsive ionization the host material should accommodate the specific ionic species and be stable under ambient conditions, be homogeneous, and be refractory to withstand the severe thermal surges inherent in the process of cyclic accumulation and emission of the energy content. Inefficiencies in the laser activation process give rise to significant thermal stresses which generally limit the power level of operation. Rare earth single crystals such as yttrium aluminum garnet $Y_3Al_5O_{12}$ (YAG), a highly stable optical material as well as a very refractory one, have a prominent position in advanced laser technology. It can be made of extremely high optical quality and the emission line width is desirably very narrow. Laser oscillation devices have been operated using YAG with a resultant spectral purity approaching that of gas dynamic lasers. An example of the four level laser system characteristic of rare earth ions is given in Figure 2.



Four-level laser system characteristic of rare earth ions.

Legend

Level 0 Ground State.

Level 1 Thermally vacant (unpopulated) at room temperature.

Level 2 Large radiative line strength between levels 1 and 2; lifetime of level 2 longer than level 1.

Level 3 Level 2 ions relaxed predominantly through radiative processes.

Figure 2. Rare earth laser diagram

There is no commercial availability of laser materials or laser devices in the U.S.S.R. with the exception of some metal drilling and cutting devices. The only population elements who are concerned with lasers are selected portions of the academic and military establishments. Funding of laser development is certainly of high level interest with one of the most senior level laser personalities, N. Basov, having been selected as a member of the Soviet parliament. This selection was an elevation in status due to his achievements and management of laser technology. There exists substantial Soviet activity in laser research and development.

2. Military Interest

The insatiable military demand for the utilization of scientific advances in improving the efficiency of potential military operations resulted in an early and sustained support for laser research development and technology. Many of the civilian and industrial uses now existent would not have been available so soon without this intellectual as well as financial support. As laser development has proceeded, the wider has become the military need for laser applications due to the extremely diverse utility of the laser in performing functions not otherwise available by other means.

The military need for rapid, secure communications in all weather conditions and over long distances is assisted through the expansion of communications capabilities and frequencies from the microwave to the optical region by a factor of over 10,000. Laser-activated communications devices are capable of generating, transmitting, and receiving enormous amounts of data in a secure mode for military battlefield use.

The narrow spectral line width of the laser beam is of importance for target designators, measuring the distance to a target, as well as for aiming a weapons system onto a target and directing a missile right onto a target up to the time of target destruction. The smart bombs are examples of a laser application. Earth satellites have had lasers mounted upon them. The use of lasers to secure rapid, extremely accurate positioning of military vehicles and equipment is increasing in importance.

The laser can be used to concentrate energy for the intensely localized heating of a target. Although originally applied to medical uses to burn away unwanted tissue or to adhere body parts not susceptible to mechanical bonding, or to drill very small holes in special parts, the laser has also been developed as a [illegible] weapon. It is possible to focus the intense monochromatic radiation on to a spot only 1/100 of a centimeter in diameter. A laser can deliver more than 100 million watts/sq cm to such a target area at short ranges within the atmosphere. This amount of locialized energy concentration is 10,000 times greater than the surface temperature of the sun and is therefore capable of melting or vaporizing the most refractory materials known.

The laser can be used in the production of vital military hardware components. For example, lasers are used to cut, trim, or modify large-scale integrated circuits which are used in computer-assisted fire control devices, in communications devices, and in missile instrumentation and control items. Devices manufactured through use of lasers are used in precision-guided battlefield missiles.

Laser active systems are in the forefront of research to achieve electrical power from nuclear fusion. The increased cost of petroleum products and other energy supplies have resulted in increased costs for military hardware and supplies. In addition, continuously stable and secure energy sources for military component and end-item manufacture must be assured. Through research on TOKOMAK devices which use lasers to initiate and continue nuclear fusion reactions a reliable energy supply can be assured. The military establishment hopes to eventually develop an internally secure, independent generating power source.

The importance of lasers for military activities is increasing rapidly as increased sophistication and efficiency are achieved. Rare earth ionic species are therefore important as they comprise a significant share of solid state laser systems of desirable attributes.

3. Materials Problems

The chief problems associated with rare earth laser materials have been:

a. Identification of quantum level concentrations of the rare earth ion required to yield laser action in a host material.

b. Securing the rare earth ion in sufficiently high purity so that impurity concentrations will not defeat the attainment of the levels of population inversion required for laser action.

c. Placement of the rare earth ion in a host material in controlled ionic concentration.

d. Securing the preparation of necessarily high-purity host materials, e.g., glass or crystals to permit adequate rare earth ion lasing action.

e. Preparation of sufficiently pure, chemically and structurally, host crystals, e.g., YAG of adequate purity and length.

4. Soviet Laser Research Program

There is an impressive amount of research being performed in the Soviet Union in the area of laser physics and quantum electronics. The scope of laser work in the U.S.S.R. encompasses a broad range of subjects, practically all of which may be concerned with the utilization of the rare earth ionic species due to their specialized electronic structures. Some of the topics which are of interest include: laser-induced thermonuclear reactions, nonlinear optics, laser spectroscopy, isotope separation with lasers, and the development of various types of lasers, including high power lasers and short wavelength lasers. Soviet scientists have made substantial contributions in the areas of semiconductor lasers, chemical lasers, and the development of lasers based upon the luminescence of crystals and glasses.

Laser research is performed at a number of centers including the P.N. Lebedev Physics Institute in Moscow, which is the Physical Institute of the Academy of Science; the Spectroscopy Institute of the Academy of Sciences; the Kurchatov Institute of Nuclear Physics; the Institute of the Physics of Semiconductors and the Institure of Automation and Electrometry, both located at Akademgorodok, the science city near Novosibirsk. There are active laser research programs at Moscow University, the Physics Institute of the Byelorussian Academy of Sciences at Minsk, the Physical Research Institute at Ashtarak, Armenia, the Ioffe Physicotechnical Institute, and the Vavilov Optical Institute in Leningrad. A listing of the chief Soviet institutions associated with rare earth oxide laser materials is given in Table 1.

Table 1. CHIEF SOVIET INSTITUTIONS ASSOCIATED WITH RARE EARTH OXIDE LASER MATERIALS

INSTITUTION	LOCATION
P. N. Lebedev Physics Institute	Moscow
Shubnikoff Institute of Crystallography	Moscow
Institute of Radio Engineering and Electronics	Moscow
N. S. Kurnakov Institute of General and Inorganic Chemistry	Moscow
Moscow State University	Moscow
Institute of Rare Metals and Alloys (Giredmet)	Moscow
Kurchatov Institute	Moscow
Institute of Magneto Dielectrics	Leningrad
Institute of Problems of Materials Management	Kiev
Vavilov Optical Institute	Leningrad

The P.N. Lebedev Institute is considered the "lead" institution in the Soviet laser program. Within this institute are located the Laboratory of Quantum Radiophysics led by Academician N.G. Basov and the Oscillation Laboratory supervised by Academician A.M. Prokhorov. Each of these laboratories has a staff of over 400 personnel (1975). There is considerable emphasis on laser physics in the Soviet Union due in great part to the leadership of Basov and Prokhorov, who shared the Nobel Prize for Physics with Charles Townes in 1964. The authority and influence of Basov and Prokhorov have been paramount in establishing the direction and priorities of Soviet laser work. The laboratory space devoted to this program is guite large. Professor Prokhorov's new (1974) laboratory building is said to be as large as the Bell Telephone Laboratories in Murray Hill, New Jersey. In the past the Soviet laser research program placed a strong emphasis on fundamental theory so that the experimental program, previously hampered by lack of facilities, is only now beginning to grow rapidly. The new laboratory facilities are consistent with our conception of the Soviet laser program as having concentrated on basic research for almost fifteen years before developing the need for more modern laboratory facilities.

The first continuous operation achieved in an optical maser or laser resulted from L.F. Johnson's work at Bell Telephone Laboratories. He was able to demonstrate a strong infrared fluorescence in calcium tungstate ($CaWO_4$) crystals doped with neodymium ions. Later in the same year, 1963, he also reported on the emission properties of the rare earth ions Nd^{3+}, Ho^{3+}, and Tm^{3+} in crystals as $CaWO_4$, $SrWO_4$, $SrMoO_4$, $CaMoO_4$, CaF_2, BaF_2, and SrF_2. It has been reported that the transparent rare earth fluorides are excellent hosts for laser action due to their exhibition of fluorescence at room temperature; and they show greater fluorescence than the other rare earth salts due to their extreme ionicity and the shielding of the 4f electrons from the crystal field. YAG is an excellent host material not only because it can be produced in extremely good optical quality but also because the spectral emission line width is very small. Laser oscillation devices have been operated using Nd^{3+}:YAG, resulting in a spectral purity approaching that of gas dynamic lasers. Following along these approaches the Soviets performed research

work in the rare earth fortified glass and single crystal systems noted. A listing of typical laser materials containing rare earth elements is shown in Table 2. Some examples of laser active systems are presented in Table 3.

An indication of the kind of basic research performed can be seen from such references as Voron'ko et al.[3] Dombrovskiy et al.,[4] and Zverev et al.,[5] wherein the direct use of the special properties of rare earth ions in producing laser action in host materials is displayed. Some of the necessary work upon studying rare earth-doped glasses is shown by Bubnov et al.[6] in noting the difficulty in controlling the structure of neodymium-doped glass rods.

Table 2. TYPICAL LASER MATERIALS CONTAINING RARE EARTH ELEMENTS

ION	HOST
Nd^{3+}.	Silicate Glass
Nd^{3+}.	Yttrium Aluminum Garnet (YAG) $Y_3Al_5O_{12}$ Crystal
Nd^{3+}.	Phosphate Glass
Nd^{3+}.	Silicophosphate Glass
Nd^{3+}.	Yttrium Aluminate ($YAlO_3$)
Dy^{3+}.	CaF_2 Crystal
Nd^{3+}.	LaF_3
Nd^{3+}.	$CaWO_4$
Nd^{3+}.	$CaMoO_4$
Dy^{3+}.	$Ca(NbO_3)$
Nd^{3+}.	$Ca_3(VO_4)_2$ YVO_4
Nd^{3+}.	$Ca_5(PO_4)_5F$ (FAP)
Nd^{3+}.	$Ca\ Y_4(SiO_4)_2O$ (Soap)
Nd^{3+}.	$Ba_2\ Mg\ Ge_2O_7$ (BMAG)

Almost every other rare earth ion has replaced Nd^{3+} and exhibited some laser action - but often with diminished efficiency.

Table 3. EXAMPLES OF LASER ACTIVE SYSTEMS

Active RE Ions	Concentration Percent	Host	Temperature deg K	Output Wavelength (Microns)
Nd^{3+}	0.14	$CaWO_4$	77-300	1.063
Nd^{3+}	0.24	CaF_2	77	1.046
Nd^{3+}	0.18	LaF_3	77-300	1.063
Nd	0.15	YAG	77	1.06
Ho^{3+}	0.5	CaF_2	77	2.09
Tm^{3+}	0.5	SrF_2	77	1.97
Er^{3+}	1.0	$CaWO_4$	77	1.72
Pr^{3+}	0.05	$CaWO_4$	77	1.61
Dy^{2+}	0.03	CaF_2	77	2.36
Eu^{3+}	0.03	$Eu(SiO_4)_3$	90	2.36
Nd^{3+}	0.15	Barium Glass	300	1.06
Gd^{3+}	0.25	LiMgAlSilicate	77	0.3125

The need for high quality glasses and crystals for doping with minor concentrations of rare earth ions gave rise to orders to other institutes to prepare such materials. The neodymium-doped glass rods used in multiple laser arrays[7] were secured from the Ioffe Institute and the Vavilov Optical Institute in Leningrad as well as from Moscow State University. High powered single and multiple beam Nd^{3+}:glass lasers have been designed and studied for some time. In 1970 the first compression experiments, a step on the way to achieve a sustainable laser fusion reaction, were carried out in Basov's laboratory at the P.N. Lebedev Institute. In these early experiments a nine-beam neodymium-glass laser was used to irradiate a spherical target of deuterated polyethylene. The laser delivered energies of the order of kilojoules for durations of several nanoseconds. In these pioneering studies Basov and Krokhin acheived a 30-fold compression accompanied by a flux of about 10^7 neutrons per pulse from the D-D fusion reaction. The Lebedev Institute has constructed a 15-kilojoule neodymium glass laser with a pulse duration of 1 to 30 nanoseconds. A feature of this work is that the scaling up of the laser power input is done through a multiple additive method whereby small cross section Nd^{3+} glass slabs produced at the Vavilov Optical Institute are placed in parallel position for building up effective beam power and for efficient cooling. The result is that geometric multiples up to over 200 slabs have been used with consequent high power concentration achieved. Some of these arrays have been in service for over a year without the need for slab replacement.

Some examples of the Soviet efforts in laser glass technology can be seen from the work at the Institute of Radio Engineering and Electronics. In a British patent Alekseev et al.[26] disclosed a special glass for use as a laser material. They claimed they had produced a high efficiency, low angular divergence laser with a chemically stable active glass element composed of:

Constitutent	Mole Percent
P_2O_5	35-49
Alkali metal oxides	1-30
Cd or Zn	20-45
Rare earth oxides	0.1-25
Al, B, Nb	0-27
ZrO_2 or Cr_2O_3	0.01-10

A specific active combination was given as P_2O_5-49.0, BaO-25.0, K_2O-19.0, Al_2O_3-5.0, and Nd_2O_3-2.0 in mole percent. The melting point was given as 1200 C with a generating spectral wave length of 1.056 microns and a microhardness of 300 kg/mm^2. This data also reveals the competence in forming a hydration-resistant glass of high structural purity. Buzhinskii et al.[27] also prepared glasses of a very low thermal expansion coefficient to avoid devitrification and the deterioration of the laser action upon repeated charging or pumping. The composition of the specific glass is given as:

Constitutent	Parts by Weight
$Zn(HPO_4)_2 \cdot 2H_2O$	59.5
$Cd(H_2PO_4)_2 \cdot 2H_2O$	49.3
$Li(H_2PO_4)$	8.55
ZrO_2	4.0
Nd_2O_3	3.5

A similar glass containing 1.5 parts Yb_2O_3 by weight was also prepared and tested for laser action. The efficiency ratio of Nd^{3+}:Yb^{3+} was found to be 1.33 at a spectral wavelength emission of 1.06 microns. These patents are indicative of a certain level of competence in dealing with the design of glasses, glass making, and test of electronic properties.

The necessity for high-quality single-crystal host materials for doping with rare earth ionic species served as a basis for extensive work upon crystal growth processes. Conventional Czochralski, Verneuil, Stockbarger, and gradient methods were diligently pursued. However, the limited size, difficulty in securing the required combination of physical, chemical, and electronic properties, as well as the sheer high cost of such material processes led to the support of Aleksandrov and a number of co-workers[8] at the P.N. Lebedev Institute in the designing, production, and utilization of a kind of ceramic crystal-growing apparatus called a "skull-melting" system. The skull-melting process consists of the direct high-frequency induction heating of the refractory material which is contained in a water-cooled crucible-formed structure. The stable melt when formed is restrained in a sintered exterior shell or skull of material of identical composition so that the problem of reaction or contamination by the crucible has been eliminated. Once formed the melt can then be cast to shape or recrystallized using more traditional processes. The advantage of being able to melt the most refractory materials is important in securing single crystals of these materials for evaluation as laser materials. The apparatus is sufficiently versatile to be used in the Czochralski crystal growth method. It is believed that Aleksandrov's group has been responsible for using this method to supply new crystals otherwise unavailable in specific dopant form for research and analysis by other institutes.

The cooperation among the various Soviet technical institutes in production, evaluation, and use of rare earth laser materials can be illustrated from the following references.[9, 10] For example, in 1975 Kh.S. Bagdasarov and A.M. Kevorkov of the Shubnikoff Institute of Crystallography coauthored a paper on $YScO_3$:Nd^{3+} crystals with A.M. Prokhorov and T.A. Tevosyan of the P.N. Lebedev Physics Institute. This work also indicates the level of competence of Kh.S. Bagdasarov, well known as a leading expert in the Soviet Union in growing single crystals of a highly sophisticated technical nature; the involvement of A.M. Kevorkov of Shubnikoff, also known for providing crystals for MHD experiments; and the interest of A.M. Prokhorov's Laboratory at the P.N. Lebedev Physics Institute in evaluating these specialized crystals. The effort among these institutions appears to be both cooperative and unified.

The apparent involvement of the Institute of High Temperatures in Moscow with rare earth laser work is indicated by the co-authorship[11] of V.A. Federov of the institution with members of the P.N. Lebedev Institute in studying the emission characteristics of neodymium in lead fluophosphate crystals.

The pervasive use of rare earth ions in Soviet laser research and development is not only due to the specific electronic properties of these ions but also to the very broad-bases, far-ranging nature of the Soviet approach to the subject. By building upon an impressive background of theoretical and applied physics, the Soviets began utilizing rare earths in laser host matrices in the 1960's.[12] This use of the rare earths has continually expanded so that now there are many programs in progress which exemplify this overly broad-gauged effort. It would appear that almost every rare earth ion and every suitable glass or crystal has been prepared and some sort of investigation performed on these materials with reference to determining laser-related properties. Typical of such investigations are publications by Kaminskiy,[13] Bagdasarov,[14,15] Voron'ko,[16] Galaktionova,[17] Zharikov,[18] Alfyorov,[19] and Dianov.[20] There are many similar studies in the same vein reported in even the most recently issued scientific journals.

Single-crystal structures which contain rare earths for laser use are suitable not only for laser action but also for laser window use for chemical and gas dynamic lasers. Therefore there is a multiple purpose for Soviet work in this area. Rare earth-activated crystal lasers have remained as an active area for several years and no diminution of this effort is evident. Arsen'yev et al.[21] studied a number of different rare earth-containing crystals (YAG, CaF_2) as recently as 1975, concluding that crystal purity and homogeneity were extremely important in such evaluations. The continued importance of crystal growth is shown by such articles as those by Bondar[22] and Leonyuk.[23] Single crystals of complex stoichiometry are being synthesized indicating an advanced state-of-the-art.

Through their widespread effort in lasers the Soviets have come across new laser materials. One example is the neodymium-activated yttrium-gadolinium aluminate system reported by Arsen'yev et al.[24] Single crystals were grown by optical zone melting in air to yield a $Y_{0.6}\,Gd_{0.35}\,Nd_{0.05}\,AlO_3$ mixture. The luminescent properties of the materials were studied at 77 K and 300 K and laser action confirmed.

The general impression obtained from the multitude of publications on rare earth compounds used in glass and crystal laser hosts is that the large Soviet Laboratories devoted to laser work have developed a capability for advanced research and development in this area with a competent support base for producing clean glass and crystals for laser use. It is believed by the Soviets that the skull-melting crystal-forming apparatus must be used as a base for Czochralski crystal growth to obtain good doped crystal structures.

The absolute amounts of rare earth compounds used are small in comparison to other materials needs and the Soviet Union is self-sufficient in this area. The other materials used in laser work are readily available. It is concluded that the level of the Soviet laser research effort is approximately equivalent to that of the United States. However, the rate of taking practical advantage of technical advances is vastly superior in the United States where technology transfer is very

rapid as compared to the sluggishness of technology transfer in the Soviet Union.[25] Table 4 lists some of the chief Soviet scientific persons associated with advanced laser research.

5. Trends and Forecast

Due in great measure to their excellent background in theoretical physics, Soviet scientists early recognized the value of rare earth ions in solid state laser research and development. Over the last decade the Soviet Union has developed on a sound basis the capability to design, formulate, and secure rare earth ions in structurally clean inorganic glasses and single crystals for study and potential use as lasers. The personnel of the P.N. Lebedev Physics Institute and the Shubnikoff Institute of Crystallography collaborated in this broad-gauged research effort, and are expected to continue as the centers for such efforts. There is continued emphasis on studying and perfecting the action of rare earth ions in solid state media for laser use. The development effort is expected to continue in the same vein of refinement over the next five years. Once the limits of laser action in these solid state lasers are perceived in comparison to the action of chemical and gas dynamic lasers, the research work in rare earth solid state lasers will level off and gradually decline. The chief emphasis will be on the use of neodymiun ion as has been the case in the United States.

The applications of rare earth ions in solid state media will not find widespread Soviet military use (as in range finders, markers, guide-in devices) for at least five to ten years, always following examples set by the United States and associated Western bloc nations, because of the very slow rate of technology transfer for such sophisticated devices. The use of multiple glass beam lasers and crystal lasers for research and development of isotope separation and nuclear fusion apparatus will continue at a rapidly developing pace in the Soviet Union because of the impetus provided by Basov and Prokhorov in these areas which are directly related to the work of the P.N. Lebedev Physics Institute. There will be a continuing effort to make structurally purer laser host glasses at the Vavilov Optical Institute and improved single crystals by V.V. Osiko and his associates at the P.N. Lebedev Institute. It is anticipated that Czochralski growth of crystals from the skull-melting furnace pioneered by Osiko will continue to be studied and refined, with careful attention to temperature gradient control.

While the Soviet scientists have gained and will continue to keep an advanced position in the research hierarchy of rare earth ion utilization in solid state lasers, it will take an unprecedented transformation in current scientific application practices for the Soviet Union to achieve widespread military and industrial uses of laser devices. There will likely be a slow but steady incremental appreciation of such devices and in time more use will be made of lasers. However, the Soviets are not unaware of lasers as potential weapons, and can be expected to increase their work in this area. It is believed that the Soviet laser weaponry lags behind the United States by about five to ten years.

In the past the Soviet Union has required only minimal quantities of rare earth compounds for laser research and spplications. It is anticipated that the Soviet Union can meet all such requirements for this purpose for at least the foreseeable future from internal resources.

Table 4. SOME OF THE SOVIET PERSONALITIES ASSOCIATED WITH RARE EARTH ELEMENT CONTAINING LASERS

Name	Institution	Field of Interest
V. I. Aleksandrov	P. N. Lebedev Physics Institute, Moscow, 1975	Growth of rare earth crystals
N. E. Alekseev	Institute of Radio Engineering & Electronics, Moscow, 1975	Nd^{3+}:PO_4 glasses
P. A. Arsenev		Rare earth aluminate laser
K. S. Bagdasarov	Shubnikoff Institute of Crystallography, Moscow, 1975	Growth, characterization, crystal structure determination of rare earth containing crystals; Czochralski method
N. G. Basov	Director, Laboratory of Quantum Physics, P. N. Lebedev Physics Institute, Moscow, 1976	Laser crystals; 9 and 20 beam Nd:Glass lasers
K. E. Bienert		Rare earth aluminate laser
L. B. Borovkova	Laboratory for Optical Properties, Shubnikoff Institute of Crystallography, Moscow, 1975	Optical property correlation with the Crystal Structures of R. E.'s w/Al_2O_3; silicates
I. M. Buzhinskii	Institute of Radio Engineering & Electronics, Moscow, 1975	Nd^{3+} glasses/PO_4 type
V. A. Danilychev	P. N. Lebedev Physics Institute, Moscow, 1976	Laser induced chemical reactions
Ye. M. Dianov	P. N. Lebedev Physics Institute, Moscow, 1975	Nd^{3+}: glass laser structures
G. F. Dobrzhaskiy	Director, Laboratory for Optical Properties, Shubnikoff Institute of Crystallography, Moscow, 1976	Crystal structure of rare earth aluminates and silicates
Ye. Ilyenskiy	P. N. Lebedev Physics Institute, Moscow, 1976	Er:YAG crystal
A. A. Kaminskiy	Shubnikoff Institute of Crystallography, Moscow, 1975	R. E. laser crystals/Laser:optical properties
A. M. Kevorkov	Shubnikoff Institute of Crystallography, Moscow, 1975	R. E. laser crystals
O. N. Krokhin	Deputy Director, P. N. Lebedev Physics Institute, Moscow	Laser induced fusion
L. A. Kulevsky	Moscow State University, Moscow	Developer of a 10kW Cd-Se parametric oscillator pumped by a CdF_2:Dy2+ laser at 2.4 microns
G. G. Malenkov	Shubnikoff Institute of Crystallography, Moscow, 1974	R. E. laser crystals (w/Bagdasarov)
N. A. Orayesky	P. N. Lebedev Physics Institute, Moscow, 1974	Laser schematic reactions
V. V. Osiko	Director, Wave Laboratory, P. N. Lebedev Physics Institute, Moscow, 1976	Growth, production of refractory rare earth containing crystals; skull melting crystal formation
I. I. Pashinin	P. N. Lebedev Physics Institute, Moscow, 1974	Apparatus-skull melting, YAG
A. G. Petrosyan	Shubnikoff Institute of Crystallography, Moscow	Slab lasers, nuclear fusion experiments
Y. I. Popov	P. N. Lebedev Physics Institute, Moscow, 1974	Rare earth containing semi-conductor lasers, laser crystals, glass lasers
A. V. Potemkin	P. N. Lebedev Physics Institute, Moscow, 1974	Rare earth aluminate laser
A. M. Porkhorov	Director, Physics Program including Oscillation Laboratory of P. N. Lebedev Physics Institute, Moscow, 1976	Lasers, laser induced chemical reactions, high energy lasers, lasers for fusion, atomic clocks
E. M. Savitskiy	Institute of Crystallography/Laboratory for Alloys of Refractory & rare metals, Baikov Institute for Metallurgy, Moscow, 1975	Laser crystals
V. H. Sakharov	Head, Institute of Rare Metals (Giredmet), Moscow, 1976	Laser work; Hd:YAG
G. V. Sklizkov	P. N. Lebedev Physics Institute, Moscow, 1976	Nd^{3+}:glass multibeam laser/fusion work
V. M. Tatarintsev	P. N. Lebedev Physics Institute, Moscow, 1976	Rare earth crystals, skull melt formation of crystals
S. G. Tresvyatskii	Institute of Problems of Materials Management, Kiev, 1975	Nd_2O_3-Al_2O_3 solid solutions
E. V. Velikov	Academician, Kurchatov Institute, Moscow, also Director Atomic Energy Institute at Krasnaya Pakhra, Moscow, 1976	Development of 32 beam laser using Nd:glass amplifiers w/IDKJ pulse power for 0.1-10 nanosecond duration
Y. K. Voron'ko	P. N. Lebedev Physics Institute, Moscow, 1975	
Yu. O. Yakovlev	Institute of Magneto Dielectrics, Leningrad, 1975	R. E. garnet crystal growth

1. SCHAWLOW, I., and TOWNES, C., *Optical Amplifiers*, US Patent 2, 929, 922, 1960.
2. JAVAN, A. *The Laser Establishment.* Laser Focus, no. 10, 1974, p. 36-44.
3. VORON'KO, Yu. K., NOBLE, E. A., OSIKO, V. V., and TIMOSHECHKIN, M. *Stimulated Emission from Electron Beam-Pumped Nd^{3+}:YAG.* Zh. Eksp. Teor. Fiz., v. 13, no. 10, 1971, p. 125-128.
4. DOMBROVSKIY, V. I., and LOMONSOV, I. I. *Radioluminescence in $Nd^{3+}:CaWO_4$ Under Intense Excitation.* Zhurnal Prikladnoy Khimii, v. 24, no. 2, 1971, p. 331-333.
5. ZVEREV, G. M., KOLODNY, G. Ya., and ONISHCHENKO, A. M. *Radioactive Transitions Between Levels of Trivalent Rare Earth Ions in YAG Crystals.* Journal of Experimental and Theoretical Physics, v. 60, no. 3, 1971, p. 920-928.
6. BUBNOV, M. M., BUZHINSKIY, Ye. M., DIANOV, Ye. M., and PROKHOROV, A. M. *Measuring Thermal Distortion in Rectangular Neodymium Glass Rods.* Kratkiye Soobshcheniya po Fizike, v. 21, no. 3, 1971, p. 7-12.
7. KUGUSHEV, A. M., GOLABEVA, N. S., and ROZHDESTVIN, M. *Synchronization of Nine Solid State Lasers.* Ivuz Radioelektronika, v. 8, no. 4, 1971, p. 363-370.
8. ALEKSANDROV, V. I., OSIKO, V. V., PROKHOROV, A. M., and TATARINTSEV, V. M. *A New Method for Obtaining Refractory Single Crystals and Fused Ceramic Materials.* Vestnik Akad. Nauk. S.S.S.R., no. 12, 1973, p. 29-39.
9. BAGDASAROV, Kh. S., KAMINSKIY, A. A., KEVORKOV, Li, L., PROKHOROV, A. M., TEVOSYAN, T. A., and SARKISOV, S. E. *Study of Stimulated Emission in Cubic Crystals of $YScO_3:Nd^{3+}$.* Akad. Nauk. S.S.S.R. Doklady, v. 224, no. 4, 1975, p. 798-801.
10. KAMINSKIY, A. A., BOGOMOLOVA, G. H., BAGDASAROV, Kh. S., and PETROSYAN, A. G. *Luminescence, Absorption, and Stimulated Emission in $Lu_3Al_5O_{12}:Nd^{3+}$ Crystals.* Optika i Spektroskopiya, v. 39, no. 6, 1975, p. 1119-1125.
11. MOROZOV, A. M., MOROZOVA, L. G., FEDEROV, V. A., and FEOFILOV, P. P. *Spontaneous and Stimulated Emission of Neodymium in Lead Fluophosphate Crystals.* Optika i Spektroskopiya, v. 39, no. 3, 1975, p. 612-614.
12. BAGDASAROV, Kh. S., and PROKHOROV, A. M. *Laser Properties of a Nd^{3+}:YAG Cation Crystal.* Akad. Nauk. S.S.S.R. Doklady, v. 212, 1968, p. 212-214.
13. KAMINSKIY, A. A. *Energy Transition Diagrams for Rare Earths in Activated Crystal Lasers.* Neorg. Mater., v. 12, no. 5, 1972, p. 904-907.
14. BAGDASAROV, Kh. S., BOGOMOLOVA, G. H., KAMINSKIY, A. A., PROKHOROV, A. M., and PROKHORTSEVA, T. M. *Laser and Spectroscopic Properties of $Gd_2(MoO_4)_3:Nd^{3+}$.* Akad. Nauk. S.S.S.R., Doklady, v. 197, no. 3, 1971, p. 557-559.
15. BAGDASAROV, Kh. S., KAMINSKIY, A. A., KEVORKOV, A. M., and PROKHOROV, A. M. *Study of Stimulated Emission from Nd^{3+} Ions in $CaScO_4$ Crystals.* Kinetika i Kataliz, v. 12, no. 7, 1974, p. 1666-1668.
16. VORON'KO, Yu. K., DINITRUK, M. V., OSIKO, V. V., and SHCHERBAKOV, I. A. *Equilibrium of Dopant Defects in $Yb^{3+}:CaF_2$ Crystals.* Fizika Tverdogo Tela, v. 198, no. 6, 1971, p. 1303-1305.
17. GALAKTIONOVA, N. M., GERSHUN, V. V., and MAK, A. A. *Single Mode C-W Nd^{3+}:YAG Laser.* Optika i Spectroskopiya, v. 37, no. 2, 1974, p. 322-325.
18. ZHARIKOV, Ye V., ZHEKOV, V. I., KULEVSKIY, L. A., MURINA, T. M., OSIKO, V. V., PROKHOROV, A. M., STARIKOV, B. P., and TIMOSHECHKIN, I. N. *Stimulated Emission of Er^{3+} Ions in YAG Crystals at 2.94 Microns.* Kvantovaya Elektronika, v. 24, no. 8, 1974, p. 1867-1869.
19. ALFYOROV, Zh. I., BILAK, V. I., GARBUZOV, N. Yu., DAVIDYUK', N. Yu., and STEL'MAKH, M. F. *Study of the Possibility of Increasing the Pulse Power of a Laser Based on Nd^{3+}: YAG with a Semi-Conductor Pump System.* Zhurnal Teknicheskay Fiziki, no. 17, 1975, p. 773-775.
20. DIANOV, Ye. M., KUTYENKOV, A. A., MANENKOV, A. A., OSIKO, V. V., PROKHOROV, A. M., RITUS, A. I., and SHCHERBAKOV, I. A. *Intensity of Rayleigh Scattering from the Metastable State of Nd^{3+} in Laser Silicate Glass.* Journal of Experimental and Theoretical Physics, v. 69, no. 2, 1975, p. 540-546.
21. ARSEN'YEV, P. A., KAMINSKIY, Ye. I., and POTEMKIN, A. V. *Evaluation of Use of Various Materials as Matrices for Active Elements of Lasers.* Kristall and Technik, v. 10, no. 6, 1975, p. 643-655.
22. BONDAR, I. A., MAMEDOV, T. G., and MEZENTSEVA, L. P. *Synthesis and Study of $Nd_yLa_{1-y}P_5O_{14}$ Single Crystals.* Kvantovaya Elektronika, no. 12, 1974, p. 2625-2628.
23. LEONYUK, N. I., PASHKOVA, A. V., and SEMENOVA, T. D. *Obtaining Aluminum Rare Earth Borate Crystals.* Neorg. Mater., no. 1, 1975, p. 181-182.
24. ARSEN'YEV, P. A., BIENERT, K. E., and POTEMKIN, A. V. *Mixed Aluminates as a New Class of Laser Materials.* Physica Status Solidii, v. 28, no. 1, 1975, p. 81-86.
25. SMITH, H. *The Russians.* Vanguard Press, New York, 1976, p. 575.
26. ALEKSEEV, N. E., BUZHINSKII, I. M., ZHABOTINSKII, V. B., RUDNITSKII, Yu. P., GAPONTSEV, V. P., and TSAPKIN, V. V. British Patent 1, 396, 452, 16 April 1973.
27. BUZHINSKII, I. M., and GAPONTSEEV, V. P. French Patent 2, 213, 244, 1974.

III. APPLICATIONS OF RARE EARTH COMPOUNDS IN EXPERIMENTAL MAGNETOHYDRODYNAMIC ELECTRICAL POWER GENERATION

1. Background

The progress in the development of modern technological nation states and their accompanying military posture may be directly associated with a continuous increase in the demand for and requirements to produce electrical energy. In the recent past the solitary event which temporarily slowed the rate of increase of electric power consumption occurred in the 1973-1975 time frame due to the staggering economic burden imposed on the West by the fourfold increase in the price of crude oil exported from members of the OPEC international oil cartel. Military requirements for least weight, high instantaneous electrical power supplied per unit volume of equipment have furnished a strong impetus for research and development of new, more efficient means of electrical power generation from conventional fuels. Modern military armaments manufacture also requires large amounts of inexpensive electrical power based upon a secure fuel supply. All these stimuli have fostered a continuing interest in the magnetohydrodynamic (MHD) method for producing electrical power within the military establishment and its assoicated research and development effort within the U.S.S.R.

The MHD method for electrical power generation consists of the direct conversion of the energy derived from an open flame operating in a magnetic field into electricity through ionizing the flame and converting the stripped electrons into electrical energy at suitable tapping electrodes.

The MHD power generating system may be divided into two broad categories of operation: the open cycle process and the closed cycle process. The basic operation of the open cycle is the evolution of a very high temperature gas gotten from the combustion of a fuel and an oxidizer, then seeding this gas with a substance which can be ionized (e.g., cesium metal) and passing the resultant plasma through the MHD channel or generator. The flow of these charged particles results in the desired current flow in the tapping electrodes so that it is thereby converted to a usable and transferable form. Rare earth compounds are used in the channels and electrodes to enhance chemical and erosion resistance while at the same time stabilizing the desired high temperature crystal structure of an oxide as zirconium oxide (ZrO_2) without reducing refractoriness. The seed material must be recovered and recycled for both economic and antipollution reasons. This type of open cycle system is a high temperature process requiring heat source temperatures of approximately 2500 C for good efficiency. Many variations have been proposed for closed cycle MHD systems. Currently, two basic types are attracting attention: liquid metal cycling and noble gas seeded with an easily ionizable gas. The liquid metal cycles operate by using a gas to absorb thermal energy from a liquid metal heat source. The compressible gas is then used to produce mechanical energy in the liquid metal which energy is subsequently converted to electrical power in the MHD generator. The noble gas cycle involves the use of a nonequilibrium gas plasma to produce electrical energy. Within the past few years major MHD research activity in Europe which had centered on coal-fired thermal reactor generators has been greatly reduced. It appeared that success was too far distant. Europe has a severe deficiency in natural gas and fossil fuel resources, and a successful MHD generator would lack cheap and secure fuel sources. Fusion power seems to

have more appeal to Western European nations. Accordingly, only minor research efforts in MHD power generation are being carried on in the OECD, as substantial government support is lacking.

The consensus of experts in the field is that open cycle MHD devices are more likely to succeed, despite the lack of realization of the severe materials problems involved. Coal is the fuel most often considered for large stations due to the large coal reserves in the United States and the U.S.S.R. Soviet scientists and engineers have used natural gas in their initial MHD reactors on account of the availability of huge natural gas reserves, the cleanliness of the exhaust gases of combustion, and because of its compositional purity which permits a better study of the MHD experiments through the minimization of fuel variability.

2. Materials Problems

There exist a number of technological material problems assoicated with MHD systems. These include the following:

a. The residual ashes from the combustion of coal must be eliminated through improved combustion chambers (e.g., cyclone chambers or multi-stage combustion techniques) or the transformation of coal to a clean fuel as achieved through gasification. Significant ash in the MHD generator channel causes erosion and corrosion, shorting out of electrodes, and the clogging of air preheaters. The seed materials cause similar difficulties but are indispensable to the process.

b. The high temperatures encountered give rise to real and significant problems in the design of long-lived channel walls and electrodes. The current density is about 10 kA/m^2, which means the electrode material must carry a current density of 10 kA/m^2 in order to preserve charge neutrality at the electrode. The requirement placed on the electrical insulation ceramic surrounding the electrode is a resistivity greater than 10 $ohms/m^3$. For a 10,000-hour lifetime an erosion rate of 5 $mg/m^2/sec^2$ or less is required. In open cycle systems an air preheater operating at temperatures of 1600 to 1800 C is needed. The preheater construction is of packed beds of dense ceramic particles. These materials undergo severe cyclic temperature changes and thermal shock fracture is a problem. In addition, the severe corrosion and erosion from reactive seed and ash materials is another factor causing structural deterioration and reduced efficiency.

c. The reactivity of the refractory channels and electrodes with the seed material also causes marked deterioration with time and can cause current conversion efficiency to be so reduced as to force reactor shutdown.

The development of improved ceramic structures of the desired high thermal conductivity, high electrical conductivity (for electrodes), low electrical conductivity, (for insulators), great thermal shock resistance, retained or improved refractoriness, and resistance to chemical corrosive attack and erosion would improve the chances for successful MHD reactor operation. Rare earth compounds, such as yttrium oxide in combination with refractory compounds such as zirconium oxide or as refractory electrically conductive oxides, have found a significant place in the attempt to solve these material problems. Typical combinations are Y_2O_3 stabilized ZrO_2 and $LaCrO_3$ and $LaCrO_3$-Cr cermet mixtures.

3. Military Interest

The interest of the military establishment in MHD power generators arose from the requirements of new advanced weapons systems. These devices require a portable, high power, fast rise time to maximum current output, light weight, and a very high current density. From a cold start to maximum power the MHD system offers the most rapid power rise time available for continuous use over long time periods. These systems could be used to power high energy laser devices and particle beam generators. The MHD systems are dry and are the lightest of all the dry systems. Therefore MHD power generation units are attractive for airborne use, especially in Army helicopters, where large amounts of weaponry power are required in ordinarily inaccessible areas under remote and severe battlefield conditions. MHD units could offer least weight per unit volume for such rapid rise time, high current density weapons requirements.

For the manufacture of military end items secure, inexpensive sources of electrical power are required. MHD electrical power generation offers an attractive solution to this problem. The military interest in rare earth compounds therefore stems from their use as crystal structure stabilizers for refractory electrode compounds and as individual compounds (as $LaCrO_3$) for channel walls.

The potential of MHD generators to provide emergency, rapid start, continuous electrical power for scattered or remote sites has not been overlooked by the military. Accordingly, the necessity for the development of such portable emergency electrical power sources is of current concern.

4. The Soviet MHD Program

The chief thrust of the U.S.S.R. MHD effort is directed toward the successful operation of an open cycle coal-fired power generation system. The products of the coal combustion process and the nature of the seeding element or compound will determine the chemical environment the critical MHD materials components must withstand. The working environment in coal-fired systems consists of high velocity hot gases (fossil fuel combustion products and alkali metal seed) with actual wall temperatures of 1500 to 1700 C. The oxygen partial pressure of the gas mixture is in the range of 10^{-4} to 10^{-2} atmospheres. The gas is a mixture of N_2, CO_2, CO, SO_2, NO_x, alkaline oxides, sulfates, and carbonates and the coal ash, primarily silica.

Soviet scientists have traditionally given high priority to finding suitable electrode materials with a secondary interest in good electrically insulating materials. For many years Soviet scientists have concentrated on the refractory electrically conductive oxides (e.g., ZrO_2 stabilized with rare earth oxides and rare earth oxides alone, as Y_2O_3) as the most suitable candidate materials for the various elements of the "hot wall" MHD generator. The refractory oxides are well suited for MHD materials because their low oxygen partial pressure and their existance in an already fully oxidized state results in a well-recognized thermal stability in air. Unfortunately, the most refractory oxides are particularly susceptible to thermal shock failure and some exhibit catastrophic crystallographic structural change upon thermal cycling. The Soviet scientists have attempted to make suitable MHD electrodes of zirconium oxide by stabilization of the crystal structure through the addition of rare earth oxides, predominantly Y_2O_3, to replace

the calcium oxide ordinarily used for the purpose. The pure zirconium oxide exhibits a polymorphic crystal structure change from monoclinic form to the tetragonal form (or high temperature stable form) at approximately 1050 C. This polymorphic transformation is reversible upon cooling so that catastrophic destruction of the structural form ensues. In addition to stabilizing the ZrO_2 in the high temperature form, Y_2O_3 and other rare earth oxide additions also assist in increasing the electrical conductivity of the electrode material over a broad temperature range. Lanthanum chromite was primarily considered as a electrode material by the Soviet scientists. Now it is also considered as a lead-out material. The rare earth compounds have therefore figured prominently in Soviet MHD materials research and development.

The Soviet Union possesses the most notable MHD program because there are three test beds in operation. The "Smart" or R-2000 reactor which used molybdenum electrodes is based at Moscow State University. The U-02 is an experimental unit believed to be located at the Institute of High Temperatures in Moscow, while the U-25 is a pilot industrial generator in the Moscow area which is reported to have fed power into the Moscow electrical grid system for short periods of time. No information is available on any planned additional installations. It would appear reasonable to suppose that a larger unit would be a logical follow-on to be constructed within the next five to seven years if the MHD generator program is to be justifed over its long and expensive history.

Within the U.S.S.R. the Soviet MHD program appears to carry a high priority of interest. Despite the apparent lack of coordination of the Soviet research institutes (with frequent duplication of effort), there is a clearly definable MHD materials program centered at the Institute of High Temperatures of the U.S.S.R. Academy of Sciences in Moscow, with visible imput from other institutions. These include the U.S.S.R. Academy of Sciences Institute of Physics (refractory oxides), Moscow State University, The Volgograd Polytechnic Institute (explosive compaction techniques), The U.S.S.R. Academy of Sciences Baykov Institute of Metallurgy (spheroid powder oxides), the UNIIO Ukrainian Scientific Research Institute (refractory cements) and the U.S.S.R. Academy of Sciences Institute on the Problems of Materials Management (Kiev) (rare earth-stabilized refractory compounds).

The Institute of High Temperatures (IHT) is largely oriented toward materials development and characterization. Much of the work involves testing and further development of materials first developed in other institutes, with some in-house developmental work. The IHT employs more than 2500 persons; about 1000 carry out physical research. The 1974 IHT annual report presents 188 as holders of advanced academic degrees, six full members of the U.S.S.R. Academy of Sciences, 24 members with doctoral degree status and 156 candidates for the PhD degree. IHT has few theoreticians but receives support from other institutes more directly concerned with materials.

As is the case in other scientific areas, the Soviets have shown a preference for a very broad-based approach to MHD materials development. They have identified categories of materials appropriate to MHD usage and then methodically studied the materials in each category. Partial success with any one material apparently never diminished the efforts with other materials. Therefore, while the Soviet scientists have not discovered any materials not known in the United States they have gathered more data on existing materials than their United States counterparts.

By way of contrast, the early success in the United States by AVCO Corporation, in using stabilized zirconia in MHD electrode applications led to greater interest in other materials for channels. Improvements in techniques for enhancing the longevity of zirconia electrodes took the form of electrode replenishment and special coatings.

The Soviet scientists have recently been attempting to develop a new material for permanent electrodes with a life of 1000 hours. In contrast, United States work had been directed toward techniques for increasing the lifetime of existing materials.

There is a significant body of technical articles by Soviet scientists on materials for potential MHD usage. Most of the information is fragmentary and incomplete. The specifications of exact test conditions are frequently inadequate and occasionally some critical parameters are not even discussed. Materials of construction are often mentioned by generic names of little direct value. The rare earth-containing materials most frequently considered include: zirconia stabilized with rare earth oxides predominantly yttria; lanthanum chromite; lanthanum hexaboride; yttrium oxide; with recent mention of single-crystal fiber-reinforced rare earth-stabilized zirconia.

The literature abounds with references on powder preparation, forming processes, sintering, phase diagram work, electrical conductivity measurements, and oxidation resistance of candidate materials for MHD use, and materials which contain rare earth as stabilizers or as the main constituent. Many of the rare earths, however, possess unstable high temperature crystallographic modifications. Lopato[20] reported an extensive investigation of phase transitions of rare earth oxides above 1800 C, and the effect of oxides of Mg, Ca, Ba, and Sr upon those polymorphic transitions at temperatures up to 2000 C. Tresvyatskii et al.[1] studied phase transformations in the Nd_2O_3-SrO system and reported on the formation of a number of new compounds in this system. The high temperature modifications of Nd_2O_3 could not be secured in a stabilized form. These papers are typical of many with some basic research presented, good in itself but not directly noted as related to MHD work.

At the IHT there has been an active program on MHD electrode materials based upon zirconia.[2,3] The thermal properties of ZrO_2 stabilized with yttria have been studied in great detail. A comparison of the data on the vaporization of refractory oxides,[4] the results of mass spectrometer study of zirconia solid solutions,[5] as well as data on the erosion resistance of refractories[6] has indicated that the use of yttria as a stabilizing additive permits very high temperatures to be sustained on the channel walls of an MHD generator for a considerable period of time without significant deterioration of operational characteristics. According to the data presented by Rekov et al.[7] the maximum use temperature of zirconia stabilized with yttria in the MHD electrode walls cannot exceed 1850 C with an ionized combustion product flow rate of 500 meters/seconds.

A recent patent by Lugin[13] and a report by Karaulov[21] illustrate a continuing interest in zirconia for MHD electrodes. Lugin patented a new material of excellent electrical conductivity of the composition in mole percent - 34-40 ZrO_2, 6-8 Y_2O_3, remainder HfO_2, as a refractory for potential MHD use. Karaulov's work

at the Ukrainian Scientific Research Institute indicates the involvement of that institution in such an endeavor, and apparent success in the complete stabilization of cubic zirconia with yttria. The successful slip casting, dry pressing, and sintering as well as the hot pressing of stabilized ZrO_2 to very high percentages of theoretical density were discussed along with analyses of the dependence of crystallite size upon firing temperature.

A recent paper by Samsonov[14] also referred to the continued interest in rare earth compounds for MHD generator usage. The wide influence of Samsonov from his base at the Institute of Problems of Materials Management at Kiev will be diminished because of his death in December 1975.

Another member of this Institute, Dubok[15] along with V.V. Lasheva patented a refractory electrically conducting electrode rare earth body composed of: 99.4-99.9 mole percent gadolinuim oxide combined with 0.1-0.6 mole percent Group II oxides. Dubok and Lashneva[16] have reported on the electrical conductivity of yttrium oxide. They investigated single crystals of Y_2O_3 as well as yttria doped with CaO and ZrO_2. They found that doping with 0.01 weight percent zirconia reduced the electrical conductivity at 1300 C by one order of magnitude while 0.15 weight percent calcium oxide increased the conductivity of yttria by two orders of magnitude. They concluded that the mechanism of action of the impurity varies as a function of the dopant in equilibrium with the oxide. This article also confirms the continued interest in rare earth oxides and their electrical properties at this Institute.

A number of rare earth oxide additives have been used by Soviet scientists to improve the temperature-resistivity characteristics of zirconia for MHD electrodes.[7] Ternary systems containing ZrO_2 were prepared with La_2O_3, CeO_2, Nd_2O_3 for comparison with a 90-10 binary ZrO_2-Y_2O_3 composition.

These kinds of ternary zirconia ceramic electrodes were reported to have been extensively tested in the U-02 MHD generator. This generator performed with power densities up to 2 kW per electrode pair and at current densities up to 2 amps/cm^2. These results were sufficiently encouraging for the Soviet scientists to commit themselves to the further development of ceramic-oxide electrodes for the U-25 installation. Current lead-out electrodes for this type of electrode were also investigated with the result that CeO_2-Nd_2O_5 and CeO_2-Ta_2O_5 compounds were found to meet the electrical resistivity and oxidation resistance requirements.[8] Solid solutions of zirconia, praseodymia, and indium oxide have also been used to fabricate new ceramic electrodes which had a practical current density limit of 4 amp/cm^2 and a maximum operating temperature of 2000 C.

The IHT has a continuing program for the production of microspheres spheroidized in a plasma torch apparatus.[22] Rare earth-stabilized zirconia powders have been prepared which reportedly do not recrystallize at temperatures below 2300 C.[9] The IHT has also produced spherical powders of ZrO_2/Y_2O_3, 50 to 200 microns in diameter. These materials are of great interest as components of high temperature air preheaters for MHD generators.[10]

Alekseenko et al.[23] in a recent study indicated the stability of zirconia stabilized with CaO and Y_2O_3. Cycling for 4 to 5 times at temperatures up to 2000 C did not change the electrical resistivity of the material. The data in the 800 to 2000 C range showed that with increased Y_2O_3 content the increases in conductivity is attributable to complexes of Y^{3+} ions. The temperature dependence of additive levels is rather flat with increased temperature. At the higher temperatures there is a slight dissociation of Y_2O_3 complexes with concomitant effects upon resistivity and thermal conductivity.

Another variation in the experimental approach to secure long-lived zirconia electrode bodies is exemplified by the use of a cermet technique. A body of the composition ZrO_2-18% CeO_2-3-5% Ta was investigated but performance results are unclear. The Soviet claim of 100% electrically conducting zirconia achieved with a number of rare earth compound additions has not been confirmed.

As part of the accessory effort to utilize rare earth-stabilized zirconia as an MHD generator material, single crystals have been prepared by scientists at the P.N. Lebedev Physics Institute under V. V. Osiko's direction and investigated by scientists at the IHT.[24] This paper is indicative of the cooperation between these institutes.

The continued interest in the preparation and properties of zirconia stabilized with rare earth oxides is exemplified by a number of recent publications by personalities long active in this area.[25-27]

The more recently examined potential MHD generator electrode materials in the U.S.S.R. include lanthanum hexaboride (LaB_6) and lanthanum chromite ($LaCrO_3$), either alone or in cermet[17,18] form. Lanthanum hexaboride is being given attention for use in porous gas-cooled electrodes.[19]

Lanthanum chromite-chromium electrodes were reported to be in good condition after 5.5 hours of operation in the U-25 generator.[8] $LaCrO_3$ had been considered for some time as a candidate material for current lead-out structures. The Soviet interest was spurred on by the success in developing an improved method for fabricating cermets based upon $LaCrO_3$.[8] $LaCrO_3$ possesses a melting point of about 2500 C, low electrical resistivity over a wide temperature range, and good oxidation resistance when doped or alloyed with other suitable materials. The Soviets have developed the temperature-resistivity curves for the $LaCrO_3$-Cr system, Figure 3. In addition, two interesting techniques were used to improve the properties of the final product:

a. The introduction of small quantities of palladium increased oxidation resistance by one to two orders of magnitude, and
b. The use of explosive compaction to increase the thermal conductivity by a factor of two to three.[7,28]

The experience with $LaCrO_3$ cermets in the U-02 apparatus has been promising enough for testing to continue in the U-25 generator.

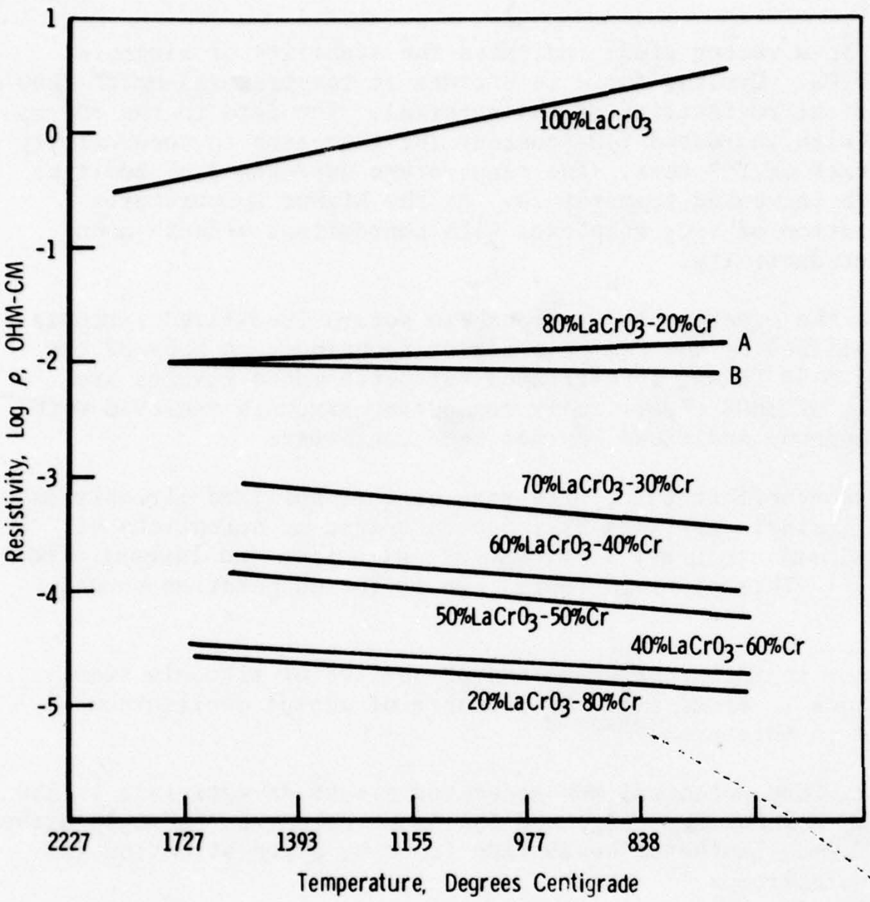


Figure 3. Resistivity data for $LaCrO_3$-Cr Combinations

The Soviets have also reported good results from adding CaO to $LaCrO_3$. The early work of Zyrin[11] demonstrated that CaO additions significantly increased the electrical conductivity of the rare earth element chromites, Figure 4. The use of CaO as an additive also appears to enhance the densification levels reached through cold pressing and sintering. With up to 5 to 10 weight percent CaO addition the open porosity could be reduced to less than 3.7%. Rekov stated that $LaCrO_3$-5 to 10 wt% CaO possesses electrical conductivity values equivalent for energy take-off from the MHD generator channel even at room temperature. However, the CaO additions did not suppress the polymorphic transformations observed by Ruiz[12] in 1967. Despite some inconsistencies in the reported data. work upon these materials is still being pursued at IHT. The IHT explosive composition method was used to prepare large thick-walled tubes as well as annular samples of $LaCrO_3$ cermets with diameters of 100 microns and wall thickness of 20 to 30 microns. This work has been followed up by Popil'skii of the Mendeleev Chemical Technical Institute.[29]

It is believed that $LaCrO_3$-Cr cermets are given primary consideration as a lead-out material because above 1500 to 1600 C the resistive surface layer growth becomes significant and would not permit long-term use as an electrode.

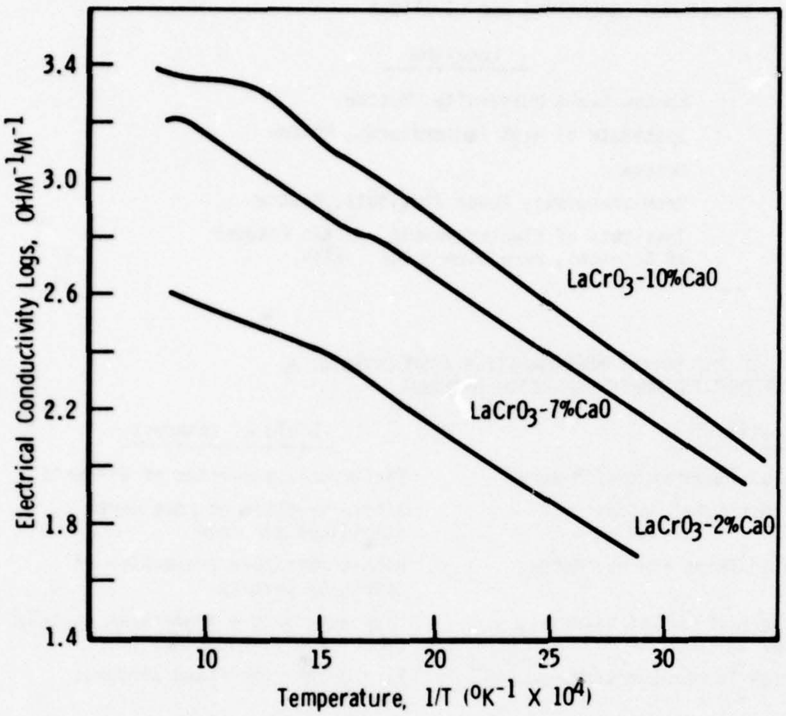


Figure 4. Conductivity versus temperature data for lanthanum chromite-calcium oxide combinations

The severity of the thermal shock/thermal stress problem for MHD generator electrode and channel materials has now forced the consideration of complex or composite ceramic structures for these uses. Ceramic fiber or single crystal whiskers have been utilized as reinforcements for ceramic bodies and to help hold bodies together after undergoing severe thermal shock which would ordinarily lead to structural failure. Publications are now appearing which indicate the use of magnesia insulator bodies and zirconia fiber to reinforce rare earth-stabilized zirconia bodies. Although research is known to be carried out on the subject, mention of direct application to MHD generator electrodes is not made.

The Institutions at which MHD work is known to be performed are given in Table 5. The locations where known and designations of Soviet MHD generators are shown in Table 6. A listing of the more prominent persons associated with MHD work in the Soviet Union is presented in Table 7.

Table 5. INSTITUTIONS ASSOCIATED WITH RARE EARTH USES FOR MAGNETOHYDRODYNAMIC GENERATOR COMPONENTS

Institute of High Temperatures of the U.S.S.R. Academy of Science, Moscow

Moscow State University, Moscow

P. N. Lebedev Institute of Physics of the U.S.S.R. Academy of Sciences, Moscow

Kharkhov Polytechnic Institute, Kharkov

Ukrainian Scientific Research Institute of Refractories, Kiev

Institute on the Problems of Materials Management, Kiev

Institute of Magneto-Dielectrics, Leningrad

Table 6. SOVIET MHD GENERATORS AND LOCATIONS

Designation	Location
R-200	Moscow State University, Moscow
U-02	Institute of High Temperatures, Moscow
U-25	Moscow
ENIN-2	Krzhizhanovskiy Power Institute, Moscow
UNKNOWN	Institute of Electrodynamics of the Academy of Sciences, Ukrainian S.S.R., Kiev

Table 7. SOME OF THE SOVIET PERSONALITIES ASSOCIATED WITH MAGNETOHYDRODYNAMIC GENERATOR MATERIALS

Name	Institution	Field of Interest
L. S. Alekseenko	Institute of High Temperatures, Moscow	Electrical properties of zirconia
V. I. Aleksandrov	P. N. Lebedev Institute, Moscow	Single crystals of rare earth stabilized zirconia
B. M. Barykin	Institute of High Temperatures, Moscow	High temperature properties of $LaCrO_3$-Cr cermets
V. A. Dubok	Institute of the Problems of Materials Management, Kiev	High temperature properties of Y_2O_3, other rare earth oxides
Ya. P. Gokhshtein	Institute of High Temperatures, Moscow	Rare earth stabilized zirconia electrodes
V. G. Gordon	Institute of High Temperatures, Moscow	High temperature properties of ZrO_2; $LaCrO_3$
A. B. Ivanov	Institute of High Temperatures, Moscow	Properties of rare earth oxides for channel use
V. A. Kirillin	Chairman, Committee for Science and Technology	Policy decisions on MHD matters
V. V. Lashneva	Institute of the Problems of Materials Management, Kiev	Electrical properties of rare earth oxides
L. M. Lopato	Institute of High Temperatures, Moscow	Polymorphism of rare earth oxides
B. V. Lukin	Institute of High Temperatures, Moscow	High temperature properties of rare earth oxides/single crystals
V. V. Osiko	Director, Wave Laboratory, P. N. Lebedev Institute, Moscow	Single crystals of rare earth stabilized zirconia
A. I. Rekov	Institute of High Temperatures, Moscow	Zirconia electrodes, $LaCrO_3$ channels
G. V. Samsonov (deceased 1975)	Institute of Problems of Materials Management, Kiev	Refractory rare earth oxides and compounds
V. Ye. Serebrennikova	Institute of High Temperatures, Moscow	Theory and practice of electrodes, channels
A. E. Sheindlin	Assistant Director Institute of High Temperatures, Moscow	MHD material - broad spectrum - policy
A. L. Spiridonov	Institute of High Temperatures, Moscow	Thermal properties of cermets
S. G. Tresvyatskii	Institute of Problems of Materials Management, Kiev	Phase transformations in rare earth oxide systems/combinations
E. P. Velikhov	Deputy Director, Kurchatov Institute of Atomic Energy, Moscow	Policy, design of MHD systems/fusion
D. A. Vysotskiy	Institute of High Temperatures, Moscow	Refractory insulating and electrode materials

5. Trends and Forecast

The early apparent resolution of the MHD generator electrode material problem through the use of stabilized zirconia by American scientists gave impetus to the Soviet interest in this material. However, after over a decade of emphasis on rare earth-stabilized zirconia, it became apparent that the material was inadequate for long-term high-temperature use. There also appeared to be no advantage in the use of other rare earth oxides in place of yttria as the stabilizing high-temperature additive. The rare earth oxides alone were unable to satisfy the stringent requirements of MHD generator electrodes. Attention then was given to $LaCrO_3$ and $LaCrO_3$-Cr cermet structures. These cermets again could not perform as electrodes but are of value as lead-out structures. The addition of small amounts of noble metals in cermet systems favorably affects oxidation resistance, but it is too expensive for any use other than experimentation. The hope of using rare earth-stabilized zirconia single crystals (called fianites) was also short-lived. Attention is now being given to fiber-reinforced composite zirconia structures containing rare earth oxides. A temporary trend away from extensive research on rare earth-containing electrode materials began about two years ago beginning with the onset of the work of the United States/U.S.S.R. MHD Materials Working Group Information Exchange Program. A hercynite-iron spinel is a strong candidate electrode material. It is believed the technical information exchange program originated because the Soviet MHD effort had failed to solve the critical electrode material problem and it was hoped that the use of United States technology could lead to a workable electrode. In addition, the advanced position of United States scientists in superconducting magnet technology (superconducting magnets are essential to MHD performance) could be taken advantage of. On the United States side, the Soviet experience with actual hardware was seen as an opportunity to use the well-seasoned Soviet test MHD generators as a test-bed for United States materials while also gaining working hardware experience. A typical MHD schematic design is shown in Figure 5.

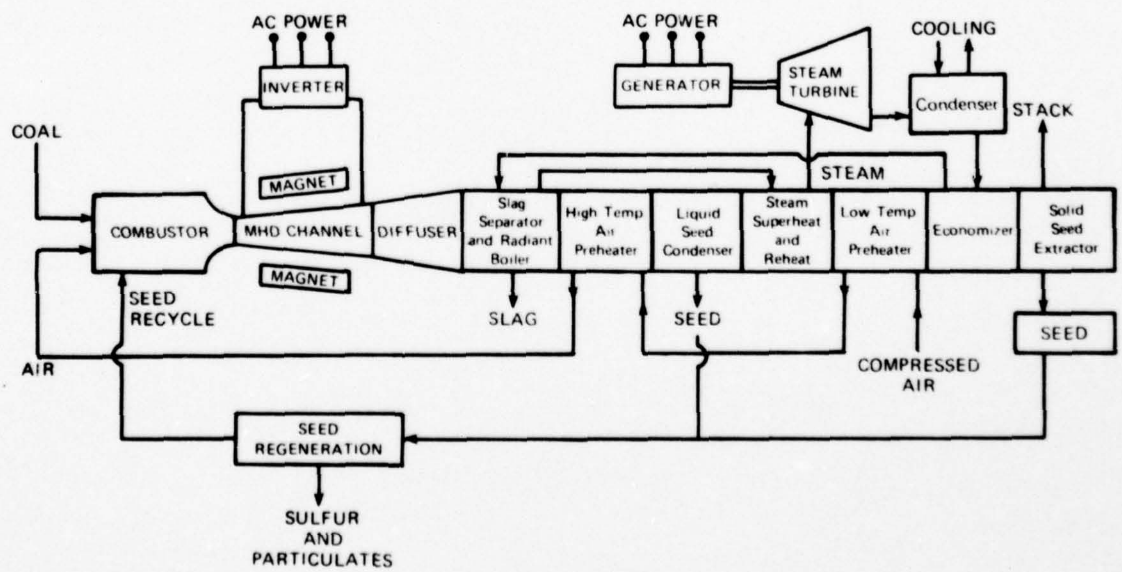


Figure 5. MHD schematic - coal fired with indirectly fired air preheater

It is believed that the high efficiencies sought for from the continuous high-temperature operation of MHD generators will not be readily achieved in the near future. The more probable likelihood is that longer term operation at lower temperatures at minimal efficiency will permit some MHD generators to be operated. This type of MHD generator operation will permit zirconia electrodes to be utilized along with the necessity for rare earth compound content. Therefore the valuable physico-chemical properties of rare earth refractory combinations (e.g., refractoriness, electrical conductivity, thermal conductivity) will cause a return to greater preeminence in their investigative use.

Fiber or whisker-reinforced composite refractory structures containing rare earth compounds will be more extensively investigated for MHD generator electrodes and channels. The combination of these composite structures with cermet technology will be of future interest to the Soviet R&D program. Although considerable progress has been made in the rare earth compound containing MHD generator materials the forecast is for slow incremental steps forward which will retain and even increase the considerable role of rare earth compound technology in MHD material application.

1. TRESVYATSKII, S. G., PAVLIKOV, V. N., LOPATO, L. M., and LUGIN, L. I. *Phase Transformations in the Nd_2O_3-SrO System.* Neorg. Mater., v. 6, no. 1, 1970, p. 41-45.
2. REKOV, A. I., ROMANOV, A. I., IVANOV, A. B., SEREBRENNIKOVA, V. Ye., and SMIRNOVA, L. G. *Magnetohydrodynamic Method of Electrical Power Production.* Energiya Press, Moscow, 1968, p. 59-67.
3. IVANOV, A. B., NABOKIKH, B. F., LUKIN, B. V., and REKOV, A. I. *MHD Generator Channel Materials.* Nauka Press, Moscow, 1969, p. 55-62.
4. TOROPOV, N. A., and BAZAKOVSKIY , V. P. *High Temperature Chemistry.* A.N.S.S.R. Press, Moscow, v. I, 1968, p. 231-242.
5. ABRAYTIS, R. I., and MAYAUSKAS, I. S. Trudy An Lit. S.S.R. Ser. B., v. 3, no. 46, 1966, p. 141-149.
6. RUTMAN, D. S., SHCHETNIKOVA, I. A., IGNATOVA, T. S., and SEMENOVA, G. L., Ogneupory, v. 69, no. 1, 1968, p. 49-55.
7. REKOV, A. I., IVANOV, A. B., LUKIN, B. V., GORDON, V. G., SEREBRENNIKOVA, V. Ye., FEDETOVA, L. I., SPIRIDONOV, E. G., and CHERNYSHOV, G. P. *Study of Open-Cycle MHD Generator Channel Electrode Wall Materials With Surface Temperature Range 1400-1850 C* in MHD Method for Producing Electrical Energy, Energiya Press, Moscow, 1972, p. 450-461.
8. SHEINDLIN, A. E. *Major Results at the Institute of High Temperatures in 1972.* Nauka Press, Moscow, 1973.
9. KIRILLIN, V. A., Proceedings of 5th International Conference on MHD Electrical Power Generation, Munich, April 1971.
10. SHEINDLIN, A. E., et al. *Major Results at the Institute of High Temperatures in 1973.* Nauka Press, Moscow, 1974.
11. ZYRIN, A. V., and DUBOK, V. A. *Chemistry of High Temperature Materials.* Nauka Press., Leningrad, 1967, p. 59.
12. RUIZ, J. S., et al. *Comptes Rendus.* Acad. Sci. Paris, Series B, v. 264, 1967, p. 1271-1274.
13. LUGIN, L. I., KUSCHEVSKII, A. E., and AKININ, K. G. U.S.S.R. Patent 435, 212, 5 July 1974.
14. SAMSONOV, G. V., MURGUZOV, M. I., and KUTSENOK, T. G. *State and Future Trends in the Development of Rare Earth Metal Group III-VI Main Sub-Group Element Compounds.* Poluchenie I. Issled Svoistv. Soedin RZM, 1975, p. 4-10.
15. DUBOK, V. A., and LASHNEVA, V. V. U.S.S.R. Patent 458, 531, 30 January 1975.
16. DUBOK, V. A., and LASHNEVA, V. V. *Electrical Conductivity of Y_2O_3.* Neorg. Mater., v. 11, no. 7, 1975, p. 1250-1255.
17. BARYKIN, B. M., GORDON, V. G., REKOV, A. I., SPIRIDINOV, A. L., and LEVINOV, B. M. *Thermal and Electrical Conductivity of $LaCrO_3$-Cr Cermets.* High Temperature-High Pressures, v. 6, no. 1, 1974, p. 47-52.
18. BARYKIN, B. M., GORDON, V. G., PROKHOROVA, I. V., and SPIRIDONOV, A. L. *Monochromatic Emittance of $LaCrO_3$-Cr Cermets Between 300 and 1900 K, in Air.* High Pressures-High Temperatures, v. 5, no. 4, 1973, p. 1393-1399.
19. ALEKSANDROV, V. I., OSIKO, V. V., MURAV'EV, E. N., SPIRIDINOV, E. G., TATARINTSEV, V. M., and GORDON, V. G. German Patent 2, 435, 657, 13 Feburary 1975.
20. LOPATO, L. M., SHEVCHENKO, A. V., KUSHCHEVSKII, A. E., and TRESVYATSKII, S. G. *Polymorphic Transitions of Rare Earth Oxides at High Temperatures.* Neorg. Mater., v. 10, no. 8, 1975, p. 1276-1281.
21. KARAULOV, A. V., and RUDYAK, G. *Sintering Zirconia with Yttrium Oxide.* Ogneupory, v. 76, no. 2, 1975, p. 54-58.
22. ASONOV, A. N., ZALESKAYA, I. M., IVANOV, A. B., KRASULIN, Yu. L., STEPANOV, V. N., and SVOBODOV, A. N. *Composition and Structure of Molten Microspheres of Stabilized Zirconia.* Ogneupory, v. 76, no. 2, 1976, p. 49-52.
23. ALEKSEENKO, L. S., KOIFMAN, G. Yu., POSOKHOVA, E. D., and SHAKHTIN, D. M. *Electrical Resistance of Stabilized Zirconia at High Temperatures.* Neorg. Mater., v. 10, no. 11, 1974, p. 2006-2008.
24. ALEKSANDROV, V. I., VAL'YANO, G. E., LUKIN, B. V., OSIKO, V. V., RAUTBART, A. E., TATARINTSEV, V. M., and FILATOVA, V. N. *Structure of Stabilized Zirconium Dioxide Single Crystals.* Neorg. Mater., v. 12, no. 2, 1976, p. 273-277.
25. GOKHSHTEIN, Ya. P., and SAFONOV, A. A. *Critical Density of the Current Across Electrodes Made from Ceramics Based Upon ZrO_2 and Rare Earth Metal Oxides.* Magnitogidrodin, Nauka Press, Moscow, 1975, p. 110-122.
26. FILATOVA, V. N., CHERNYSHOV, G. P., VAL'YANO, G. E., PANKRIAT'EVA, G. Y., RAUTBORT, A. E., LUKIN, B. V., REKOV, A. I., and AKOPOV, F. A. *Ternary ZrO_2 Solid Solutions.* Neorg. Mater., v. 11, no. 8, 1975, p. 1427-1429.
27. GOKHSHTEIN, Ya. P., SAFONOV, A. A., and LIUBIMOV, V. D. *Physicochemical Behavior of MHD Generator Electrodes Made from ZrO_2-Y_2O_3 and ZrO-CeO_2 Ceramics.* Magnitogidrodin Metod. Poluch. Elektroenergii, v. 3, no. 4, 1972, p. 328-347.
28. ATROSHCHENKO, E. S., KRASULIN, Yu. L., LIPOVATYL, B. I., SEDYKH, V. S., and SPIRIDONOV, F. G. *Explosive Compacting of Electrical Materials.* Tr. Volgograd. Politekh. Inst., v. 4, no. 3, 1972, p. 229-237.
29. POPIL'SKII, R. Ya. *Synthesis and Sintering of $LaCrO_3$-CaO Mixtures.* Neorg. Mater., v. 10, no. 3, 1974, p. 50-54.
30. METUSHEVSKIY, A. S. *Facility for Testing Fiber Crystals.* Zavodskays Lab., no 1, 1972, p. 17-19.
31. TASKAYEV, I. P. *On the Whisker Growth Mechanism.* Fizika i Khimika Obratoki Materialov, v. 42, no. 3, 1972, p. 62-64.

IV. YTTRIUM ALUMINUM GARNET

1. Background

Yttrium aluminum garnet (YAG) is a single-crystal substance of sufficient importance to be treated separately in this study. Yttrium aluminum garnet now serves important technological purposes and the potential for continuous future usage is great. The chemical formular $Y_3Al_5O_{12}$ would indicate a complex inorganic molecule as well as a complex crystal structure. The material is hard, greater than 8.5 on the mhos scale of hardness, and in pure form possesses a clarity or transparency coupled with a very high refractive index which gives rise to an appearance similar to a diamond gemstone. One use to which single-crystal YAG has been put is as a jewel or synthetic diamond in the jewelry trade.

The electronic crystal structure of YAG is such that it can readily perform as a host material for various metallic ions, in particular for neodymium 3+ and other rare earth ions which can exhibit laser and other microwave properties of promising efficiencies. Typically small percentages of Nd^{3+} ion (0.5%) properly dispersed in a YAG single-crystal host lattice exhibits certain electronic properties which make it useful for microwave applications. In addition, YAG can be used as a substrate for certain integrated microcircuits containing many hundreds of electronic semiconductor elements. YAG crystals may also be doped with all of the rare earth ions with varying effects upon line widths, emission spectra, and efficiency of operation.

Single-crystal YAG which has a melting point of approximately 1950 C is generally formed through use of the Czochralski method from melts of high purity materials contained in noble metal crucibles. However, the indicated volume growth rates are low and due to the temperature severity the required equipment is expensive to construct and maintain. Therefore the absolute cost of high-purity electronic-grade YAG is high and shape availability is low. Significant amounts of research resources are being expended to gain YAG crystals of high purity and great crystal structure perfection in order to achieve certain electronic properties in the final crystal shape.

2. Military Significance

Advanced military electronic hardware requires many types of support components which may utilize YAG or specially doped YAG as a critical material item. Laser designator-rangefinders will employ Nd^{3+}:YAG parts. Multiple-ganged Nd^{3+}: YAG crystals will be used as the critical components on multibeam high energy laser weapons systems. YAG crystals may well be used as substrates and components of electronic computer control circuits for fire power control, as parts of electro-optic devices for electronic beams upon which advanced missiles can home in to targets, as parts of laser communications systems, as parts for initiating electronic signals into fiber optic secure communications devices and for initiating control commands into certain remote control weapons systems. Microwave electro-optic devices now being developed will use YAG as a critical component material. The use of YAG in large-scale integrated circuit devices for computer memory and control circuits will make possible miniaturized computers for multipurpose military uses, e.g., for intruder detection and analysis.

3. Soviet Activities in YAG

There has been a significant interest in YAG by Soviet scientists for over a decade. A large amount of research work has been performed on the production and analysis of YAG crystals for laser use by leading Soviet scientists at the P.N. Lebedev Physics Institute, the Shubnikoff Institute of Crystallography, the Institute of Power, and Moscow State University. The examples of the most recent work are presented here as they are indicative of the current state of advancement of YAG in the Soviet Union. In general, the Shubnikoff Institute and the P.N. Lebedev Physics Institute are the suppliers of the best YAG for research use.

Dianov et al.[1] studied and reported on the specific transitional cross sections and absolute quantum yield of neodymium 3+ ions in YAG crystals. The emission spectrum included the strongest line at 1.06 microns. The crystals were supplied from within the P.N. Lebedev Institute. Kaminskii[2] also reported on the problems (e.g., inhomogeneities, lack of properly pure ionic states) of the transition electronic states and crystal states of Nd^{3+} doped YAG crystals. He indicated the problems of securing reproducibly doped crystal structures with consistent emission spectra efficiency (e.g., laser action).

Petrosyan, Bagdasarov et al.[3] of the Shubnikoff Institute of Crystallography remarked upon the problems associated with different single-crystal formation conditions upon the distribution coefficient for neodymium 3+ ions in the YAG single-crystal lattice. The Nd^{3+}:YAG crystals were prepared bv the Czochralski method and a gradient tube furnace method. The latter method utilizes a variation of temperature gradients in order to supply different crystallization conditions. In another publication Bagdasarov et al.[4] stated the growth conditions for YAG were studied. The purity of the raw materials employed to produce the YAG crystals is indicative of the level of purity available in rare earth oxides within the Soviet Union. The starting melt employed 99.999% Y_2O_3, and 99.99% Al_2O_3 with activating additives of 0.3 to 1.0 weight percent Nd_2O_3 and Cr_2O_3. For temperature gradients of less than ten degrees per millimeter a finely divided granular mixture of $YAlO_3$ and $Y_3Al_5O_{12}$ was gotten. At a temperature gradient range between 10 and 13°/mm, crystallites of YAG were formed from the melt. However, as the temperature gradient was increased, the absolute YAG/$YAlO_3$ ratio decreased. At temperature gradients greater than 300°/mm, cracking and twinning of single crystals occurred. The important temperature gradient data for yielding good YAG crystals was not made available. However, it was claimed that YAG crystals 12 mm in diameter by 50 mm long were produced. Dianov et al.[5] of Academician Prokhorov's Laboratory at the P.N. Lebedev Physics Institute have reported the direct measurements of laser action in Nd^{3+}:YAG crystals. Kaminskii[6,7] has reported on the spectrospic behavioral properties of YAG both alone and in a multibeam arrangement. He noted the existence of a device employing a number of laser crystals ganged together for laser action to form the "multibeam" laser. The critical details of rare earth ion dopant efficiencies were not provided.

It is worth noting that Kaminskii et al.[8,9] have explored the use of many of the rare earth ions in a YAG host lattice and have reported on the specific electronic transition states. In cooperation with A.M. Prokhorov's Laboratory at the P.N. Lebedev Physics Institute, rare earth aluminum garnets doped with various rare earth ions as scandium, lutetium, gadolinium, erbium, neodymium,

thulium, and holmium were prepared and evaluated as active media for solid state lasers. Quantum yields and spectroscopic emission line data were elicited, indicating the wide choice of wavelengths available in these systems. The most efficient and consistent emission was obtained with Nd^{3+} emitting at a principal wavelength of 1.06 microns.

Arsenev and Bienert[10] of the Institute of Energy have prepared mixed aluminate single crystals by the optical zone melting method in air. Single crystals of Gd^{3+} and Nd^{3+} doped YAG were grown and studied. The spectroscopic investigations involved light absorption, luminescence, and lifetime decay measurements on a Nd^{3+} concentration series and at different mixing ratios of the solid solution components. The theoretical calculation of the Nd states in the mixed aluminates was performed with a BESM-4 computer.

Ashurov et al.[11] and Benderskii et al.[12] have reported on typical activation experiments utilizing not only different ionic activators but also a solid solution host crystal of mixed rare earth composition YAG-GAG.

These papers are typical of a great many in the literature concerning rare earth activators of YAG host crystals. Although we are dealing with very specific electronic structures of doped single-crystal YAG and isomorphs, the details of equipment, Czochralski seed crystal pulling rates, means for obtaining precise furnace temperature gradients and other significant aspects of single-crystal growth, the data needed for verification experiments is apparently just a little bit out of reach. However, the importance attached to single-crystal growth of rare earth doped YAG single crystals is attested to by the number of publications by significant personalities attached to important Soviet research and development institutions. The conclusions are that the potential for laser weaponry and computer and communications applications is seen as important by Soviet scientific policy makers. The chief Soviet personalities associated with YAG work are presented in Table 8.

Table 8. SOVIET PERSONALITIES ASSOCIATED WITH YTTRIUM ALUMINUM GARNET WORK

Names	Institution	Field of Interest
P. A. Arsenev	Institute of Energy, Moscow, 1974	Nd^{3+}:YAG spectroscopy
Kh. S. Bagdasarov	Shubnikoff Institute of Crystallography, Moscow, 1975	YAG crystal growth
E. M. Dianov	P. N. Lebedev Physics Institute, Moscow, 1975	Physical measurements of YAG efficiency
A. A. Kaminskii	P. N. Lebedev Physics Institute, Moscow, 1975	YAG growth and evaluation
A. M. Kevorkov	Shubnikoff Institute of Crystallography, Moscow, 1975	YAG growth and evaluation
A. G. Petrosyan	Shubnikoff Institute of Crystallography, Moscow, 1975	YAG crystal growth
A. M. Prokhorov	P. N. Lebedev Physics Institute, Moscow, 1975	YAG policy - scientific reviewer

4. Trends and Forecast

From modest beginnings over a decade ago, but based upon sound theoretical and practical capacities of Soviet scientists knowledgeable in both physics, crystal growth, and crystallography, there has been a steadily accelerating effort

with significant supportive resources attached to making YAG crystals for military electronic applications. Some of the most prestigious institutions such as the P.N. Lebedev Physics Institute and the Shubnikoff Institute of Crystallography have been involved. From one method only, the Czochralski method of crystal growth, Soviet scientists have developed and are performing numerous experiments with: skull melting; directional gradient crystallization; optical zone melting; to produce high-quality rare earth-containing single crystals with a primary emphasis on Nd^{3+} doped YAG. The trend is toward more sophisticated equipment, and more variation in types of crystal growth. However, this effort is indicative that the goal of development of mass production of these specialized crystals has not yet been achieved. The problem of securing large crystals of reproducible well-defined emission properties has not been solved.

Despite the continued emphasis on the area of YAG crystal growth, electronic property control, and size availability, the advent of success will be very slow and we can look for continued allocation of Soviet resources in this important area. Due to this deficiency YAG for laser devices will not be readily available for use in any large quantity for at least five years. It is therefore concluded that deployment of laser range finders for Soviet troops will not be possible at least until the early years of the next decade. Should there be noted a diminution of the reports of the research effort within the next two or three years, it would be an indication that some success had been achieved and would warrant more extensive and continuous investigation.

There will be continued emphasis on other methods of crystal growth, the details of which are well worth gathering because of the interest of United States scientists engaged in important crystal growth projects.

1. DIANOV, E. M., KARASIK, A. Ya., KUTENKOV, A. A., NEUSTRUEV, V. B., and SCHERBAKOV, I. A. *Lasing Transition Cross Sections and Absolute Quantum Yield from the Metastable State of Neodymium (3+) Ion $4f^{3/2}$ in Laser Glasses and Garnet Crystals.* Kvantovaya Electron, v. 3, no. 1, 1976, p. 168-173.
2. KAMINSKII, A. A. *Problems of Stimulated Emission Spectroscopy of Nd^{3+} Activated YAG Crystals.* V. SB. Spectroskopiya Kristallov, v. 14, no. 2, 1975, p. 92-122.
3. PETROSYAN, A. G., BAGDASAROV, Kh. S., BUTAEVA, T. I., KEVORKOV, A. M., SHAKNAYZARYAN, A. A. *Effect of Crystallization Conditions on the Distribution Coefficient for Neodymium (3+) Ions in YAG Single Crystals.* Kristallografiya, v. 20, no. 5, 1975, p. 109-190.
4. BAGDASAROV, Kh. S. KEVORKOV, A. M., and PETROSYAN, A. G. *Growth of YAG Single Crystals by the Directed Crystallization Method.* Kristallografiya, v. 20, no. 4, 1975, p. 877-891.
5. DIANOV, E. M., KARASIK, A. Ya., NEUSTRUEV, V. B., PROKHOROV, A. M., and SCHERBAKOV, I. A. *Direct Measurements of Luminescence Quantum Yield from the $NF^{3/2}$ Nd^{3+} State in YAG Crystals.* Dokl. Akad. Nauk S.S.S.R., v. 224, no. 1, 1975, p. 64-67.
6. KAMINSKII, A. A., BOGOMOLOVA, G. A., and KEVORKOV, A. M. *Spectroscopic Studies of Crystals with the Garnet Structure.* Neorg. Mater., v. 11, no. 5, 1975, p. 884-889.
7. KAMINSKII, A. A. *Multibeam Lasers.* Neorg. Mater., v. 10, no. 12, 1974, p. 2230-2231.
8. KAMINSKII, A. A., SOBOLEV, B. P., BAGDASAROV, Kh. S., KEVORKOV, A. M., FEDOROV, P. P., and SARKISOV, S. E. *Stimulated Emission of the $4f^{3/2}$ Transition of Nd^{3+} Ions in Crystals.* Phys. Stat. Solidi A, v. 26, no. 1, 1974, p. K63-65.
9. BAGDASAROV, Kh. S., KAMINSKII, A. A., KEVORKOV, A. M., and PROKHOROV, A. M. *Rare Earth (3+) Ion Additives as Active Media for Solid State Lasers.* Dokl. Akad Nauk Phys., v. 218, no. 4, 1974, p. 810-813.
10. ARSENEV, P. A., BIENERT, K., and POTEMKIN, A. V. *Spectroscopic Investigation of Neodymium in Mixed Aluminates of Yttrium and Gadolinium.* Phys. Stat. Solidii A, v. 33, no. 2, 1976, p. 511-515.
11. ASHUROV, M. Kh., BATYGOV, S. Kh., and DENKEV, B. I. *Effect of Temperature on the X-Ray Luminescence of Doubly Activated YAG Crystals.* Kratk. Soobshch. Fiz., v. 26, no. 11, 1973, p. 22-27.
12. BENDERSKII, L. A., VEDEKHIN, A. F., TOPCHIEV, G. M., and KLIMINA. Z. P. *Synthesis and Luminescence of Solid Solutions in the Cerium Activated $Y_3Al_5O_{12}$-$Gd_3Al_5O_{12}$ Systems.* IZV Akad Nauk. S.S.S.R., Ser. Fiz., v. 38, no. 6, 1974, p. 1205-1206.

V. YTTRIUM IRON GARNET

1. Background

A class of ceramic materials, known as the ferrites, has found important applications in radar and microwave communication systems. The ferrites are composed of iron oxide combined with one or more metal oxides to yield structures possessing ferrimagnetic properties. Of the many varieties of ferrites, yttrium iron garnet (YIG) is the best material for many electronic circuit design components and has become the ferrite material most widely used in microwave physics and engineering.

YIG does not occur in nature. It was synthetically developed in 1956. YIG is made from ferric oxide and yttrium oxide in proportions represented by the chemical formula $3Y_2O_3 \cdot Fe_2O_3$. Polycrystalline YIG is synthesized as a powder, pressed to shape and fired at about 1400 C in a controlled atmosphere to retain stoichiometry. Single crystals of YIG can be grown in a platinum crucible using a flux of lead fluoride and lead oxide which forms a molten solution with the yttrium and iron oxides. The crucible is heated to 1300 C, cooled very slowly at about one degree per hour to 1000 C, then cooled or quenched suddenly to prevent resolution of the YIG crystals. The single crystals of YIG are found embedded in the cooled mass. Separation is accomplished by selective solution of the flux in dilute acetic acid and nitric acid. YIG has been crystallized on a seed crystal from a molten $BaO\text{-}B_2O_3$ solution by slow cooling in a melt in which a rapidly rotating YIG seed crystal is suspended. YIG crystals have also been formed on a rotating seed crystal placed in the cooler portion of a crucible with a designed temperature gradient.

Microwave circuits must make use of waveguides or related transmission devices in place of the wiring used for the lower frequencies employed in broadcast radio or television circuits. Radar equipment uses YIG as an important part of the radar transmission system in the form of a circulator. In this use, it can transmit radiofrequency energy in one direction of rotation but not the other. It is used to protect the radio frequency power tubes from sudden changes in transmission line impedance, and to use the same antenna for reception and transmission. YIG microwave circulators are produced to cover frequency ranges from 0.2 to 24 gigacycles (24,000 megacycles) per second.

Single-crystal YIG is utilized to control the higher frequencies in many modern electronic circuits. This work began in the early 1960's and has expanded rapidly. The single-crystal YIG is used for microwave filters and limiters and for microwave delay systems. In a frequency range that extends from VHF radio to visible light, the gyromagnetic effects of YIG are characterized by high volume resistivity, narrow line widths, and low saturation magnetization. A small YIG sphere, about 0.05 inch in diameter, placed between an input and output transmission line, is resonant over a decade (10:1 frequency ratio) and can be tuned by varying the strength of an external magnetic field applied perpendicularly to the transmission lines. With good quality crystals and a very highly polished surface, the selectivity of these devices is very high. Some microwave tunable filters with as many as six stages have been developed. Each succeeding stage increases the overall selectivity of the circuit by rejecting unwanted frequencies. These devices are of tremendous importance for the production of high quality communications systems.

Single-crystal YIG is of extensive importance as a component of sophisticated electronic computer systems. It is an active subject of advanced research for bubble domain device based computer circuitry. YIG is also of value as a substrate and for components of integrated optical devices.

2. Military Interest

Polycrystalline and single-crystal yttrium iron garnet is extremely important for both present and future military electronic hardware because of the specialized functions it can supply. The military receivers for battlefield use such as "walkie-talkies," electronic detection devices, battlefield unit communications transmitters and receivers, especially the variable frequency type, and secure communications devices, all utilize YIG in one or more forms or components. The potential for microminiaturization of on-board fire power control minicomputers is enhanced by the use of YIG for magnetic bubble device technology. Single-crystal substrates are needed to grow a thin-film YIG magnetic garnet epitaxially upon a nonmagnetic substrate material closely matching the lattice constant chemistry and physical structure of the material to be deposited. Incidentally, the most useful substrate material and the one used exclusively in developing systems is gadolinium gallium garnet (GGG). This crystal has been grown by the Czochralski process.

Other uses of YIG components include computer-controlled guidance systems, military radar devices, and specialized component parts of electronic countermeasure devices. The dependence of military radar systems upon YIG products is both specific and essential.

3. Recent Soviet Work

Within the past five years the Soviet scientists concerned with the research and development of YIG have performed a sound piece of work in establishing the means for preparation (e.g., crystal growth) and the study of such crystals for advanced technological purposes. There has been strong interest in this area at the Moscow State University, the Shubnikoff Institute of Crystallography and the Moscow Power Energy Institute.

It is important to note that the materials for investigation are prepared by each organization separately, so that even the electronic engineers possess captive crystal growth operations.

Balbashov and Korotun[1] of the Moscow Power Energy Institute reported on the experimental parameters for growing YIG by the Czochralski process. Using a radiant energy source they described their method of operation and concluded that such rare earth ferrites must be grown at pressures equal to or less than 30 atmospheres of oxygen. It was reported this method was capable of growing rare earth:FeO_3 type crystals in any gaseous medium including high pressure pure oxygen. Balbashov, Tsvetkova et al.[2] determined the temperature and concentration field in a YIG melt formed by the radiant heating method. The growth conditions for the removal of crystals from the melt were determined, and the mechanism of the precipitation of the alpha-Fe_2O_3 phase was studied. Single crystals of YIG free of inclusions were precipitated from the melt by varying the temperature of the

melt--but not exceeding either the eutectic or peritectic temperatures. The partial pressure of oxygen over the melt was 15 to 20 atmospheres. Balbashov has also published with Cervenkis[3] work on epitaxial thin films of YIG and other uses of YIG in electronic device technology.

Belov,[4] Gapeev, and associated scientists at Moscow State University have carried on an active program on YIG for the past few years. The program is quite basic in nature, but it also is indicative of the level of sophistication of academic persons in this field. Belov and Tretyakov[5] reviewed exchange interactions with rare earths, helicoidal structures, magnetic anisotropy in YIG, magnetostriction, rare earth ferrites with the garnet structure, anomalous coercive force, orthoferrites, transitions in the antiferromagnetic state, and some allied subjects. Belov et al.[6] reported on spin flip transitions in YIG-type materials and produced a magnetic phase diagram for the terbium-yttrium iron garnet system. Over the temperature range of 80 K to 200 K the magnetic susceptibility, Young's modulus, and torque were determined for the $Tb_xY_{3-x}Fe_5O_{12}$ system. The predominant effect is a change of the principal direction of magnetization from the [111] plane to the [100] plane. The theoretical values of K_1 and K_2 as calculated agreed with the physical phase diagram. Belov et al.,[6] Gapeev et al.,[7] and Belov et al.[8] have covered a wide ranging study of YIG and associated compounds indicating continued interest in the subject.

Dudorov et al.[9] reported on a method for growing films of YIG garnets with a uniform thickness and a low density of defects. There was no evaluation of electronic properties although it may be considered that with the enhanced perfection of structure, the properties of interest would be quite good; such a material could be an excellent candidate for substrate applications. In another paper Talanin et al.[10] discussed the optimum conditions for the growth yield of homogeneous YIG films with a regular domain structure from supercooled solutions in a PbO-B_2O_3 melt. Complex garnet films of the composition $Y_3(Ga,Fe)_5O_{12}$, $(Y,Sm)_3(Fe,Ga)_5O_{12}$ and $(Y,Er)_3(Fe,Ga)_5O_{12}$ were grown. Some static magnetic properties and characteristics of the films were obtained. These films would be good candidates for computer components.

Shur and Khrabov studied the magnetic properties of YIG and $YFeO_3$ single-crystal powders.[11] In the 0.25 to 1400 micron size range portions of the powders are remanently thermally magnetized thereby producing a metastable domain structure. Some particles are single domains while others have a multi-domain structure. Therefore one can explain why there are areas of easy and difficult magnetization.

Yu.M. Yakovlev of the Institute of Magnetodielectrics has published widely in the YIG field of interest. His main work was published with S. Gendelev on "Ferrite Single Crystals in Radioelectronics."[12] His work on cylindrical magnetic domains (CMD) is classic. He and his co-workers have studied the stability of cylindrical magnetic domains in YIG as well as in $TmFeO_3$, $LuFeO_3$, $GdFeO_3$, $YFeO_3$, and complex crystals as $Sm_{0.55}Tb_{0.55}FeO_3$, and $Eu_2ErGa_{0.6}Fe_{4.4}O_{12}$ and presented data on the temperature and field dependence of the CMD formation and collapse diameters, and CMD collapse field and magnetization behavior. Stripe domains were also encountered in these materials. The best thermal stability of CMD was found in $LuFeO_3$. CMDs in $YFeO_3$ were stable with a CMD diameter of 90

microns and a domain wall velocity of 6000 cm/sec-Oersted. The connection of Yakovlev's work to computer information technology is given by his papers with others.[13,14] It would appear that there is adjuvant work performed at this Institute to support the extensive evaluations of such specialized single-crystal ferrites.

There are continuing fundamental property investigations on YIG. Selivanova et al.[15] studied the conditions for the reduction of YIG under equilibrium conditions and through the use of X-ray diffraction analysis found that in the 800 C to 1100 C range oxygen is eliminated from YIG in three steps using a steam-hydrogen atmosphere. The first step is: YIG reduces to $YFeO_3$ and wustite, then the wustite and hydrogen give rise to Fe plus H_2O, and finally the $YFeO_3$ plus hydrogen yield Y_2O_3, iron and water.

The brief reference in 1971 by Boyarchenkov[16] as an active participant in magnetic bubble domain research is not followed by subsequent references to him. As the senior author he would appear to be a man of some importance in YIG bubble domain work. Additional data on his work would seem to be desirable. The chief Soviet personalities associated with YIG research and development are presented in Table 9.

Table 9. PERSONS ASSOCIATED WITH SOVIET YIG RESEARCH AND DEVELOPMENT

Name	Institution	Field of Interest
K. S. Bagdasarov	Shubnikoff Institute of Crystallography, Moscow, 1975	Growth, characterization, crystal structure of YIG Czochralski method
A. M. Balbashov	Moscow Power Energy Institute, Moscow, 1975	R&D garnet crystals
K. P. Belov	Moscow State University, Moscow, 1975	Magnetic materials
M. A. Boyarchenkov	Institute of Electronic Computer Control, Moscow, 1975	YIG, orthoferrites, bubble domains
V. N. Dudorov	Moscow State University, Moscow, 1975	Growth of YIG films
N. V. Fabrikov	P. N. Lebedev Physics Institute, Moscow, 1975	Garnet crystal growth, Czochralski method, R. E. orthoferrites
S. Sh. Gendeev	Institute of Radio-Electronics, Moscow, 1975	Ferrite single crystals in radio electronics
Ye. Ilyashenko	Institute of Automatic Control Problems Computer Control, Moscow, 1975	YIG crystal, substrates, magnetic bubble technology for memory systems
V. V. Lemonov	Ioffe Physico-Technical Institute, Leningrad, 1974	YIG electronics research
F. V. Lisovskii	Ioffe Physico-Technical Institute, Leningrad, 1974	Magneto-optical effects in YIG
B. V. Mill	Moscow State University, Moscow, 1975	Growth of YIG films
V. K. Rayev	Laboratory of Magnetic Domain Devices, Institute of Electronic Computer Control, Moscow, 1975	YIG crystals, bubble domain work
Ya. S. Shur	P. N. Lebedev Physics Institute, Moscow, 1975	Magnetic Properties of YIG
Yu. D. Tretyakov	P. N. Lebedev Physics Institute, Moscow, 1974	R. E. magnetic materials, bubble domain garnets
Yu. O. Yakovlev	Institute of Magnetodielectrics, Leningrad, 1975	R. E. garnet crystal growth and evaluation
N. K. Yushin	Ioffe Physico-Technical Institute, Leningrad, 1974	YIG electronic research

4. Trends and Forecast

Although ferrites had interested Soviet scientists for some years, the effort and sophistication of institute work in the area indicates that great importance is attached to support of this area. The obvious military interest in the subject and the lack of reports on actual applications, especially for actual radar and computer use, indicates that this type of work is being primarily performed in Soviet military scientific establishments. The work of educational scientific workers will continue to be available on the fundamental properties of such specialized electronic crystals as YIG. However, the military applications can only be followed indirectly. Increased basic studies of YIG by the technical institutes can be expected.

In view of the fact that Soviet scientists are active in similar YIG research areas as are counterparts in this country, it may be assumed that they have the same type of advanced computer and radar end items in mind. It is doubtful that the rapid technology transfer to precision manufacturing in YIG crystal growth and device application can be accomplished within the next five years. Therefore, there will be a continuation of the attempts of the Soviet Union to purchase this technology from United States sources.

1. BALBASHOV, A. M., and KOROTUN, M. M. *Conditions for Growing Single Crystals of High Melting Substances by the Czochralski Method by Radiation Heating.* Izv. Akad. Nauk. S.S.R. Ser. Fiz., v. 39, no. 1, 1975, p. 222-224.
2. BALBASHOV, A. M., TSVETKOVA, A. A., and CHERVONENKIS, A. Ya. *Defect Nature of YIG Crystals Grown from a Non-Stoichiometric Melt.* Neorg. Mater., v. 11, no. 1, 1975, p. 108-111.
3. BALBASHOV, A. M., and CERVENKIS, A. *New Life in Science and Technology* in Radio, Electronics, and Communications Series No. 9, Magnetic Crystals in Technology, Moscow, 1975, 64 pages.
4. BELOV, K. P., and SOKOLOV, V. I. *Magnetic and Electronic Investigations of Ferrites* in MGU, Moscow, 1971, 42 pages.
5. BELOV, K. P., and TRETYAKOV, Yu. D. *Development of the Study of the Physics of Rare Earth Magnetic Materials in the U.S.S.R.* Izd. Mosk. Univ., Ferrimagnetism, 1975, p. 5-18.
6. BELOV, K. P., ZVEDIN, A. K., LEVITIN, R. Z., MARKOSYAN, A. S., MILL, B. V., MUKHIN, A. A., and PEROV, A. P. *Spin Flip Transitions in Cubic Magnets-Magnetic Phase Diagram of Terbium-Yttrium Ferrite Garnets.* Zh. Eksp. Teor. Fiz., v. 68, no. 3, 1975, p. 1189-1212.
7. GAPEEV, A. R., LEVITIN, R. Z., MARKOSYAN, A. S., MILL, B. V., and PEREKALINA, A. A. *Magnetic Properties of YIG.* Soviet Physics JETP, v. 40, no. 1, 1974, p. 117-119.
8. BELOV, K. P., GAPEEV, A. R., LEVITIN, R. Z., MARKOSYAN, A. S., and POPOV, Yu. F. *Magnetic Anisotropy and Magnetostriction of Yttrium Iron Garnets.* Soviet Physics JETP, v. 41, no. 1, 1975, p. 117-121.
9. DUDOROV, V. N., MILL, B. V., and TELESNIN, R. V. *Growth of YIG Films from Supercooled Melts.* Fiz. Fak. Mosk. Gos. Univ. Prib. Tekh. Eksp., v. 21, no. 2, 1974, p. 245-247.
10. TALANIN, R. V., DUDOROV, V. N., and KOZLOV, V. I. *Growth, Magnetic Properties and Domain Structure of Epitaxial Films of Magneto-Uniaxial Garnets.* Fiz. Tverd. Tela., v. 17, no. 7, 1975, p. 2072-2075.
11. SHUR, Ya. S., and KHRABOV, V. I. *Magnetic Properties of YIG and $YFeO_3$ Single Crystal Powders.* Zh. Eksp. Teor. Fiz., v. 68, no. 2, 1975, p. 727-735.
12. YAKOVLEV, Yu. M., and GENDELEV, S. Sh. *Ferrite Single Crystals in Radio-Electronics* in Sov. Radio and Moscow, U.S.S.R., 1975, 360 pages.
13. YAKOVLEV, Yu. M., VINNIK, M. A., and RUBALSKAYA, E. V. *Preparation and Properties of Single Crystals of Magnetic Semi-Conductors.* Fiz. Magn. Yavlenii Mater. Vses, v. 7, 1973, p. 44-55.
14. YAKOVLEV, Yu. M., MATVEEV, G. A., FILONICK, V. S., and DEVYATOVA, T. A. *Cylindrical Magnetic Domains in Uniaxial Single Crystal Materials as Information Carriers.* Fiz. Tverd. Tela., v. 18, no. 3, 1976, p. 1062-1066.
15. SELIVANOVA, T. I., BALBASHOV, A. M., VOROBEV, Yu. P., MEN, A. N., and TOMILOV, I. P. *Reduction of Yttrium Iron Garnet $Y_3Fe_5O_{12}$ Under Equilibrium Conditions.* Zh. Fiz. Khim., v. 49, no. 4, 1975, p. 867-870.
16. BOYARCHENKOV, M. A., RAEV, V. K., SAMARIN, M. I., and BALBASHOV, A. M. *Magnetostatic Interactions in Some Bubble Domain Propagation Circuits* in Digest of the International Magnetic Conference, IEEE, New York, N. Y., 1971, one page.

VI. REFRACTORIES

1. Background

Rare earth oxides as well as rare earth sulfides and nitrides have long been known to possess highly refractory properties. In essence, the temperature stability of rare earth oxides makes them suitable for use where high melting point materials are required. The melting points of rare earth oxides are well above the 2000 C range and these oxides are also possessors of high free energies of formation, thereby indicative of relatively low vapor pressures and concomitant stability.

The most economic and therefore the most familiar uses of the rare earth oxides as refractories have been as additives to improve upon or extend the usefulness of classical refractory materials. In some cases rare earth oxides have proven economic or unique in their usefulness for certain tasks. Crucibles of yttrium oxide are used to reduce uranium from uranium oxide; yttria crucibles are used to melt samarium-cobalt or other rare earth alloys from which rare earth (RE) Co_5 supermagnets are made. Y_2O_3 is useful as a refractory coating, as a wash for molds and crucibles to contain exotic alloys, as a wear-resistant surface on metal extrusion dies, as a release agent in sophisticated alloy casting, as a brazing stop, as a die facing or as a fiber coating in fiber-metal composite technology. The rare earth oxides can be plasma sprayed onto other oxides, as alumina, to form inert coatings. Yttralox is a special case refractory, wherein the addition of ten percent thoria facilitates the complete densification of yttria into a form which is transparent throughout the visible spectrum and far into the infrared (8000 nm), as well as refractory (mp, 2050 C). Transparent lanthanum oxide and cerium oxide have been similarly obtained through press forging. Crucibles of rare earth compounds are suitable for melting metals, for example, aluminum, and for evaporating them in vacuo.

As an additive, 10 weight percent Y_2O_3 stabilizes zirconia (in various forms from shapes to coatings to textiles) against catastrophic self destruction due to changes in the crystal lattice upon thermal cycling. Up to 15 weight percent rare earth oxides in a magnesia composition is used to make fused shapes for BOF steelmaking furnaces. The refractoriness and inertness are required for superior resistance to erosion and corrosion by the high lime content slag characteristic of modern steelmaking. Up to 15 weight percent rare earth oxides are used in zirconia-alumina glass tank refractories to upgrade their resistance to wear, thermal shock, high temperatures, blistering, and stoning. Several variations of yttria-stabilized zirconia have been developed for special properties. One type with a small percentage of mullite achieves the extra strength and density needed in dies for copper and aluminum extrusion. Another type of transparent zirconia is able to transmit visible and infrared radiation for use as arc lamp envelopes, scanning domes, fuel cells, furnace windows, or coatings for other refractories. In addition, only yttria and yttria-rare earth-stabilized zirconia possess the long-duration high-temperature stability for super-high temperature heat exchangers. This type of zirconia has been found to be useful at temperatures up to 2350 C.

An important potential use for rare earth oxides, particularly yttrium oxide, is in stabilizing zirconia for refractory bricks for high-temperature long-term use in steelmaking and in glassmaking.

2. Military Interest

The chief military interest in rare earth-containing refractories consists in their use for supportive activities. There is a potentially direct application in the MHD field as refractory channel and electrode components, or as potential missile antenna windows and radomes for missile systems. The need for refractories to melt superconducting alloys for special magnets for MHD device components is an important application.

Special refractories such as stabilized zirconia are employed in high temperature furnaces (both as a refractory and as insulation) used to produce parts for military equipment. These high temperature materials, e.g., rare earth-stabilized zirconia, are used in high temperature heat exchangers for hypersonic wind tunnels used to test aircraft and missile structures.

The development of means to process titanium through vacuum induction heating could be made possible through use of Y_2O_3 as a crucible or as a mold for casting titanium or for a mold facing. This would permit the use of essentially the same technology to process titanium as is presently used for casting superalloys. This might permit the long-delayed introduction of titanium into a multitude of high-strength, low-weight military components.

Refractory zirconia felts have a potential use in jet engine insulation. Small percentages of Y_2O_3 introduced into the refractory structural material silicon nitride have markedly improved the high temperature performance of the material. Rare earth-containing oxides also have found use as fuel cell components. The use of zirconia refractories stabilized with rare earths permits the production of optical glass for military use thereby performing an indirect but necessary function. Rare earths are therefore an often unnoticed yet essential part of refractories to support military end-item production.

3. Recent Soviet Work in Rare Earth-Containing Refractories

The traditional emphasis of the Soviet research effort in refractory materials has been predominantly directed toward conventional materials for the ferrous and nonferrous metallurgical industry and this emphasis upon silica, chamotte, high alumina, and periclase refractories is still evident. The Soviet refractories industry was able to fulfill the ninth Five-Year Target Plan ahead of schedule in honor of the 25th Congress of the Communist Party of the Soviet Union. The growth in the past decade in the Soviet refractories industry was accompanied by the development and production of new (for the Soviet Union) types of high-quality alumina-based refractories. There was an increase in the volume and diversity of these refractory products. Efficient production practices were instituted to increase the durability and longevity of thermal processing equipment and to accomplish the lessened consumption of refractories per ton of steel. These new products include noncrumbling Dinas (silica), chamotte, kaolin and mullite refractories, thermal insulation products of fibrous high alumina compositions for use in high temperature regenerators for blast furnaces, as well as magnesite, periclase, and zirconia slabs for the slide gates of steel casting ladles.

The tenth Five-Year Plan for the refractories industry included a pure oxides division of the Semiluk magnesia plant indicative of an increased knowledge of and sophistication in refractories production. The utility of rare earth oxides in upgrading special refractories was not noted. It was claimed that research results are now available to improve the technology for pure oxides, for sinterable alpha alumina, for stabilized zirconia products for chemical plants and for heating elements to be produced from stabilized zirconia useful for service under oxidizing conditions up to 2200 C. These heating elements are considered to contain significant amounts of a rare earth oxide as yttrium oxide.

The Soviet research institutes have utilized rare earths to stabilize zirconium oxide in the high temperature stable form for many years. It is of interest to note that references are made to the United States work in the fields of zirconia stabilization, both as a scientific reference and as a seeming justification for the work program. The chief institutions concerned with rare earth-containing refractories are contained in Table 10.

Table 10. INSTITUTIONS CONCERNED WITH RARE EARTH-CONTAINING REFRACTORIES

All-Union Institute of Refractories
I. V. Grebenshchikov Institute of Silicate Chemistry, Moscow
Institute of High Temperatures, Moscow
S. M. Kirov Polytechnical Institute, Eastern Institute of Refractories, Ural
D. I. Mendeleev Institute of Chemical Technology, Moscow
Ukrainian Scientific Research Institute for Refractories, Kiev
Institute of Problems of Materials Management, Kiev

The Ukrainian Refractories Institute[1] recently reported on a photometric method for the rapid determination of yttrium in zirconia refractories. The method required the solution, separation, and determination as well as estimates of accuracy of the determinations in the 0.5% to 15% range. This work was an accessory to the work of Rudyak and Karaulov[2,3] concerning the sintering of zirconia as a function of the crystal structure stabilizer, and also sintering zirconia with yttria to form dense bodies. The work of Gogotskii et al.[4] also showed that dense refractory structures could be obtained from yttria and magnesia stabilization of zirconia. The continuation of work on rare earth-stabilized zirconia indicates the desired direction of the effort to establish zirconia as a useful refractory for high temperature furnaces and for MHD purposes.

Karaulov et al.[5] and his co-workers have shown that the kinetics of the formation of cubic phases in zirconia and hafnia is concentration dependent. In particular, cubic phases as determined by X-ray diffraction begin to form at 700 C in ZrO_2 and HfO_2, and 100% transformation is obtained at 1750 C with six percent Y_2O_3 for the ZrO_2 refractory; ten percent Y_2O_3 is required to fully convert HfO_2 to the desired cubic crystalline form.

The personnel at the Institute of the Problems of Materials Science in Kiev have systematically investigated reactions of rare earth oxides with magnesia and calcia to improve the chemical and hydration resistance and still retain the high

temperature stability of these refractory materials. Gerasimyuk et al.[6] studied the formation of $CaLn_4O_7$ and $CaLn_2O_4$. The existence of $Ca_3Yb_2O_6$ and $Ca_2Yb_2O_5$ indicates the complexity of these systems and the necessity of determining the phase diagrams and regions of crystal stability for such compounds. These compounds can be very refractory, melting points in the 1800 to 2200 C range, but changes in crystal structure are indicative of instabilities which may rule out these materials as candidates for industrial use. Ogorodnikova and Lopato,[7] following on more than a decade of study of rare earth oxide-magnesia systems, confirmed the applicability of the theory of regular solutions to this class of oxide systems through a direct comparison of theory with the experimental phase diagrams.

These systems, e.g., Dy_2O_3-MgO, Y_2O_3-MgO, Nd_2O_3-MgO, Sm_2O_3-MgO, Dy_2O_3-MgO, and La_2O_3-MgO all exhibit liquidus points in the 1900 to 2100 C range. In these ranges the theory was able to predict eutectic points within 10 to 60 degrees C. This result is important for further consideration of these materials as refractories.

A recent paper by Lukin and his co-workers[8] at the D.I. Mendeleev Chemico-technological Institute in Moscow remarks upon the wide usage of materials in the special refractories industry based upon solid solutions of ZrO_2 with up to 15 to 20 mole percent Y_2O_3. It was also claimed that solid solutions of Y_2O_3 with up to 10 mole percent ZrO_2 can become optically transparent when produced to theoretical density. Their study consisted of powder synthesis of the raw materials (indications of the high purities available are: 99.99% Y_2O_3 and 99.6% ZrO_2), specimen formation and X-ray diffraction analysis, strength measurements and a check upon the stability of $Y_2O_3 \cdot 2\ ZrO_2$ in agreement with other values for yttrium zirconate. The authors noted that the material exhibited a room temperature strength of 1300 kg/cm^2. This flexural strength value increased with a rise in testing temperature. At 1000 C the strength level rose to 1320 kg/cm^2, at 1200 C it rose to 1910 kg/cm^2, and finally lessened to 1610 kg/cm^2 at 1300 C. The increase of strength with temperature is interesting, but the causes are not yet known. At elevated temperatures this material did not show any reaction with molybdenum.

The long-term interest in rare earth ceramics of potential refratory use by D.N. Poluboyarinov and his co-workers at the D.I. Mendeleev Institute is shown by a report[9] on the creep of yttrium oxide-based ceramics. Dr. Poluboyarinov had been involved with rare earth oxide research for at least 25 years at the D.I. Mendeleev Institute. This paper stated the lack of data on creep of yttria ceramics was a gap that required filling due to the very important structural requirements for yttria ceramics. The important result was that the creep rate of a ceramic body obtained from pure Y_2O_3 (MARK Y-00 of 99.99% purity) was lower than pure alumina. Additions of Al_2O_3 and ZrO_2 were found to be detrimental to the creep rate of pure yttria. An important investigation of the Y_2O_3-HfO_2-SiO_2 system was performed by Parfenenkov et al.[10]

The intrinsic refractoriness of Nd_2O_3, melting point 2315 C, led Kascheev et al.[11] at the S.M. Kirov Polytechnical Institute and the Ural division of the Eastern Institute of Refractories to consider it as a candidate material for industrial use. They found that vacuum firing to 1800 C produced the optimum density (porosity, about one percent) and structure. The feasibility of using

neodymia ceramics in very high temperature apparati was investigated by plaque tests in contact with tungsten and molybdenum in vacuo at temperatures up to 2000 C with a one-hour holding time. No interaction occurred between Nd_2O_3 and the metals involved. Unfortunately, the hydration resistance of Nd_2O_3 is similar to that of CaO. Well-sintered flawless specimens crumble along the available surfaces so that destructive hydration occurs within a matter of days. Further consideration of Nd_2O_3 would require means for hydration stabilization and protection or continuous use at dry, elevated temperatures, and accepting a sacrificial loss when the material is cooled to room temperature.

The problem of structurally undesirable phase transformations in rare earth oxides has been addressed by Lopato et al.[12] at the Institute of Problems in Materials Science in Kiev. It had been previously established that rare earth oxides in which the cations possessing the 3+ oxidation state exist in five polymorphic forms: two hexagonal forms A and H, a monoclinic form B, and two cubic forms C and X. The crystallization of a rare earth oxide in a particular structural form is governed by the temperature level and the size of the ionic radii of the rare earth cations. This work resulted in the correction of Foex' diagrams of rare earth oxide phase transitions at very high temperatures. Through additions of the divalent cations Mg, Ca, Sr, and Ba in oxide form it was found that at temperatures greater than 1800 C oxides of the yttrium subgroup may exist in the A and B polymorphic forms, and oxides of Tb, Dy, and Y may also exhibit the X form. The significance of this paper is the demonstration of sophistication in high-temperature rare earth oxide technology and in revealing the complexity of crystal structure transformations occurring some few hundred degrees below the melting points of these oxides. The divalent cation additions of Ca and Sr extended the regions of existence of certain crystal modifications while the effect of Mg and Ba was negligible. The authors did confirm the relevance of crystal chemistry-phase diagram association work in predicting the elevated temperature behavior and stability of these potentially useful refractory oxides.

Smirnyi et al.[13] reported the production of useful refractory articles by the deposition of powders in a high temperature gas flame. Among other oxides they reported the utility of the method for Y_2O_3 as well as for yttrium and neodymium zirconates. It was possible for the authors to produce bars, tubes, bowls, slabs, and crucibles of these materials. However, only alumina-based refractory shapes were displayed in an accompanying photograph and although the authors claimed the relevance of the method for rare earth oxides it is unlikely that the rare earth-based products were of high quality. The temperatures of deposition of 1850 to 2800 C are noteworthy in view of the apparent simplicity of the apparatus described. No tests or evaluations were carried out upon the rare earth-containing articles.

The emphasis on the use of rare earths to stabilize zirconia and hafnia is shown by two recent Soviet patents. Karaulov[14] used 6 to 8% Y_2O_3 plus CaO and a particle size of the additive of less than 8 microns to prepare a stable zirconia grain. Articles were made by grinding the grain to less than 3 microns, with 80% less than 2 microns. Other items were slip cast and fired to at least 1750 C using 94 mole percent HfO_2 plus 6 mole percent Y_2O_3; an apparent density of 9.48 to 9.56 was obtained, which corresponds to a 2 to 4% porosity. The material was able to withstand a number of 20 to 2000 C cycles. Another recent patent[15]

describes a zirconia formulation containing neodymia and chromia which exhibits excellent temperature stability and resistance to thermal fluctuations. A melting point of 2330 C was reported for a Nd_2CrO_3 additive. A mixture of ZrO_2 and Nd_2O_3 was fired to 1750 C to produce a cubic structure solid solution. This powder was mixed with Cr_2O_3 (90% of the particulate of a particle size below one micron) and fired at 1700 C. A refractory composition of 82 mole percent ZrO_2, 11.3 mole percent Nd_2O_3, and 6.7 mole percent Cr_2O_3 withstood 17 cycles of quenching from 1300 C into chilled water before fissures appeared.

In recent years there has developed in the refractories industry a tendency to utilize microspheres and microballons (hollow microspheres) as a filler for heat resisting and thermal insulation materials. Reports have been made on microspheres of varied compositional structures and sizes in the production of refractory bricks, refractory castable cements, thermal insulation for vacuum furnaces, for flue pipe lining, and for composites. The use of microspheres permits very lightweight bricks of high refractoriness to be obtained. Asonov and co-workers[16] at the High Temperature Institute developed a plasma-spray process using commercial-grade pure zirconia powder (MRTU-6-06, No. 965-63) and yttria powder grade I-1 (RETU 1072-69) to produce stabilized zirconia microspheres, using 8.7 mole percent Y_2O_3. Both fine and coarse powder fractions were processed and spheroidized up to a 250-micron diameter sphere. The production of a granulated fractionated material in the form of microspheres by treatment in a high frequency electric discharge unit makes it possible to dispense with production operations like fine grinding, briquetting or pressing, and firing and crushing of the briquets in the production of these high-temperature-resistant granular fillers. Products like this are not available in the United States except on a laboratory preparation basis.

The apparently low volatility in vacuo of rare earth compounds led to the study of a number of magnesia-yttria refractory combinations by Kaibicheva and co-workers[17] at the S.M. Kirov Polytechnical Institute. They covered the range from pure magnesia to 65.3% Y_2O_3 content (to yield 3 $MgO \cdot Y_2O_3$). These materials were found to be stable and exhibited less than one percent weight loss for exposure times up to 20 hours at 1700 C. Their interest in vacuum furnace refractories may be related to the vacuum casting of steel. The possibility exists that these people may also be interested in casting titanium. The more prominent people concerned with rare earth refractory work in the Soviet Union are listed in Table 11.

The use of rare earth oxides in so many different places and by a number of Soviet research workers still has not resulted in a significant large quantity use in the Soviet refractories industry.

4. Trends and Forecast

With the heavy emphasis of Soviet workers on refractories for steel production, there has been very little actual use of rare earth oxides in the Soviet industrial machine. The use of rare earth oxides as additives to stabilize zirconia is important to note as the Soviets were not satisfied with calcium oxide-stabilized zirconia products due in part to the very high thermal expansion which calcia-stabilized zirconia exhibits. This property leads to the rapid cracking of zirconia refractories subjected to thermal cycling. Therefore the use of Y_2O_3 which stabilizes zirconia with less of an absolute thermal expansion increase

Table 11. SOVIET PERSONALITIES ASSOCIATED WITH RARE EARTH REFRACTORIES RESEARCH IN THE SOVIET UNION

Name	Institution	Field of Interest
V. I. Aleksandrov	P. N. Lebedev Physics Institute, Moscow, 1976	Fusion synthesis of rare earth crystals/powders
A. N. Asonov	High Temperature Institute, Moscow, 1975	Rare earth stabilized zirconia microspheres
L. B. Borovkova	D. I. Mendeleev Chemico-Technical Institute, Moscow, 1975	Y_2O_3 stabilized zirconia
V. B. Glushkova	Institute of High Temperatures, Moscow, 1975	Rare earth oxide stabilization of zirconia
A. B. Ivanov	Institute of High Temperatures, Moscow, 1975	Rare earth oxides; REO stabilization of ZrO_2
M. N. Kaibicheva	S. M. Kirov, Polytechnical Institute, Uralsk, 1976	Periclase Y_2O_3 materials
A. G. Karaulov	Ukrainian Scientific Institute for Refractories, Kiev, 1975	Stabilization and sintering of ZrO_2 w/rare earths
Yu. L. Krasulin	Institute of High Temperatures, Moscow, 1975	Rare earth (Y_2O_3) stabilized ZrO_2 microspheres
L. M. Lopato	Institute of Problems of Materials Management, Kiev, 1975	Reactions of rare earth oxides with oxides
E. S. Lukin	D. I. Mendeleev Moscow Chemico-Technical Institute, 1975	Y_2O_3 stabilized ZrO_2
V. V. Osiko	P. N. Lebedev Physics Institute, Moscow, 1976	Fusion synthesis of rare earth crystals/powders
V. N. Parfenenkov	I. V. Grebenshchikov Kiev Institute of Chemico-Technical Silicate Chemistry, Moscow, 1975	Solid solutions of Y_2O_3-HfO_2-SiO_2 for high temperature use
D. N. Poluboyarinov (deceased 1975)	D. I. Mendeleev, Institute of Chemical Technology, Moscow, 1975	Sintering of rare earth oxides, especially Y_2O_3, ZrO_2-Y_2O_3
I. N. Rudyak	Ukrainian Scientific Institute for Refractories, Kiev, 1975	Y_2O_3 stabilized ZrO_2
G. V. Samsonov (deceased 1975)	Institute of Problems of Materials Management, Kiev, 1975	Multiple uses of rare earth oxides
E. M. Savitskii	Institute of High Temperatures, Moscow, 1975	Y_2O_3 stabilized zirconia
V. M. Tatarintsev	P. N. Lebedev Physics Institute, Moscow, 1976	Synthesis of rare earth crystals/powders
S. G. Tresvyatskii	Institute of Problems of Materials Management, Kiev, 1975	Reactions of rare earths with oxides

appears more suitable. The path which United States refractories workers took was to only partially stabilize zirconia so that while some monoclinic zirconia remains in the final fired structure the overall thermal expansion is lessened and longer survival results. The use of rare earth-stabilized zirconia is increasing with the expansion of the chemical industry where zirconia is required for resisting basic processing conditions. The Soviets are likely to use more rare earth-stabilized zirconia than the United States in practice.

Although the two senior men, G.V. Samsonov and D.N. Poluboyarinov, who published widely on rare earth research in refractories, died in December 1975, it is expected that their successors will continue the same types of semi-basic research. That is, the work is basic in character but can be readily applied by experts if some industrial use develops.

Continued work on using rare earth oxides to stabilize zirconia and as an additive to magnesia can be expected in view of the trend toward the basic oxygen furnace to more efficiently prepare high quality steels. These super refractories have the potential for permitting longer campaigns before furnace rebuilding is necessitated. It is believed that the Soviet metallurgists are interested in casting titanium and it is possible that rare earth oxides are being used in this work either as crucibles, mold liners, or mold washes.

Continued institute research and development work on rare earth-containing refractories can be expected, but no real advances over the United States state of knowledge in the field can be expected. If a significant use of rare earths in the United States develops, it can be expected that the Soviet workers will follow the development closely.

Continued research work on rare earth oxide phase diagrams, crystal structures, and physical and chemical properties is to be expected. This area should be watched in case a crucible material for titanium shows promise. The need for better crucibles to melt and to evaporate both readily available and exotic metals will provide an impetus for the investigation of rare earth oxide-metal interactions to serve as a basis for potential practical usage.

1. KOROBKA, L. A., TRETYAK, Z. A., DANILOV, I. P., and IVANOVA, G. M. *Photometric Determination of Yttrium in Zirconia Refractories.* Ogneupory, v. 16, no. 4, 1975, p. 239-241.
2. RUDYAK, I. N., and KARAULOV, A. G. *Sintering of Zirconia as a Function of the Stabilizer Concentration.* Ogneupory, v. 13, no. 10, 1972, p. 663-666.
3. KARAULOV, A. G., and RUDYAK, I. N. *Sintering Zirconia with Yttria.* Ogneupory, v. 16, no. 2, 1975, p. 123-127.
4. GOGOTSKII, G. A., KUKOLEV, E. V., GASHCHENKO, A. G., KARAULOV, A. G., RUDYAK, I. N., DOBROVOLSKIY, V. I., and VED, V. Ye. *Investigation of the Heat Resistance and Reliability Properties of Zirconium Oxide Stabilized by Yttrium Oxide and Magnesial Refractory Materials.* Neorg. Mater., v. 9, no. 11, 1973, p. 2067-2073.
5. KARAULOV, A. G., RUDYAK, I. N., TARANUKHA, N. M., and GLUSHKO, L. I. *Formation of Solid Solutions of Yttria with Zirconia and Hafnia.* Neorg. Mater., v. 10, no. 7, 1974, p. 1098-1119.
6. GERASIMYUK, G. I., ZAITSEVA, Z. A., LOPATO, E. M., and TRESVYATSKII, S. G. *Reactions of Rare Earth Oxides of the Yttrium Subgroup with Calcium Oxide.* Neorg. Mater., v. 9, no. 10, 1973, p. 1566-1568.
7. OGORODNIKOVA, A. A., and LOPATO, L. M. *Calculation of the Phase Field Boundaries in the Systems Ln_2O_3-MgO.* Neorg. Mater., v. 9, no. 11, 1973, p. 1723-1727.
8. LUKIN, E. S., BOROVKOVA, L. B., and KHUDAK, E. B. *Some Properties of the Ceramic with the Composition Y_2O_3-$2ZrO_2$.* Neorg. Mater., v. 10, no. 10, 1974, p. 1643-1644.
9. BOROOKA, L. B., LUKIN, E. S., POLUBOYARINOV, D. N., BAKUNOV, V. S., and RYABTSEV, K. I. *Creep of Yttrium Oxide-Based Ceramics.* Neorg. Mater., v. 10, no. 5, 1975, p. 812-813.
10. PARFENENKOV, V. N., GREBENSHCHIKOV, R. G., and DOMANSKII, A. I. *Solid Solutions in the System Y_2O_3-HfO_2-SiO_2.* Neorg. Mater., v. 10, no. 6, 1974, p. 999-1022.
11. KASCHEEV, I. D., MAMYKIN, P. S., EMLINA, M. E., and KOKSHAROV, V. D. *The Sintering of Neodymia.* Ogneupory, v. 16, no. 10, 1975, p. 588-591.
12. LOPATO, L. M., SHEVCHENKO, A. V., KUSHCHEVSKII, A. E., and TRESVYATSKII, S. G. *Polymorphic Transitions of Rare Earth Oxides at High Temperatures.* Neorg. Mater., v. 10, no. 8, 1974, p. 1276-1280.
13. SMIRNYI, V. V., DELAROVA, N. I., RYABOV, A. N., DUBROVINA, E. P., and GLUSHKOVA, V. B. *Refractories Production by Gas-Flame Deposition from Pure High-Melting Oxides and Their Compounds.* Ogneupory, v. 16, no. 2, 1976, p. 120-122.
14. KARAULOV, A. G., and TARANUKHA, N. I. *Stabilized HfO_2 Refractories.* U.S.S.R. Patent 707,624.
15. SHAPLYGIN, G. *Zirconia Based Refractory Composition.* U.S.S.R. Patent 873,850.
16. ASONOV, A. N., ZALESKAYA, I. M., IVANOV, A. B., KRASULIN, Yu. L., STEPANOV, V. N., and SVOBODOV, A. N. *Composition and Structure of Fused Microspheres of Stabilized Zirconia.* Ogneupory, v. 16, no. 2, 1976, p. 114-116.
17. KAIBICHEVA, M. N., KAMENSKIKH, V. A., and GILEV, Yu. P. *Properties and Structure of Periclase-Yttria Materials.* Ogneupory, v. 16, no. 1, 1976, p. 52-54.

VII. RARE EARTH OXIDES IN GLASS SYSTEMS

1. Background

The rare earth oxides have been used in silicate glasses for many decades. Because of their electronic shell structure with incomplete inner electron shells, rare earth ions exhibit relatively narrow absorption and emission spectra in the $4f^{3/2}$ state of oxidation in silicate glasses. The function of rare earth oxides in glass is that of a colorant, with combinations of rare earth oxides either acting as a pigment or as a solution color. In special circumstances the incident radiation can transform the electronic state of rare earth ions in glass from a transparent to an opaque ionic configuration, thereby giving rise to the phenomenon of photochromism.

The rare earth oxides, when used in appropriate form, can perform as chemical and physical decolorizers for commercial glasses. The presence of cerium oxide in bulk glass can chemically assist the decolorization of the glass by converting the residual iron content from ferric to the colorless ferrous ion. Other rare earth ions such as neodymium and erbium act as physical decolorizers through adding a spectral complement to the ferric ion, neutralizing its color. The result is a grayish cast imparted to the bulk glass without loss in clarity. Cerium oxide may also act to keep other decolorizers as Se and Mn in the desired valence state during the melting and fining of commercial glass batches. The amounts of rare earth oxides used to perform these functions are relatively small, but the results are of importance to glass makers.

2. Military Interest

There is a direct military interest in the use of rare earth oxide decolorized glass for vehicle windows, nonglare glasses for vital instrument lenses, and for transparent armor. The tinting of glass to make nonglare lenses for instrumentation use is performed with rare earth oxides either alone or as a combination grouping known as didymium. The addition of rare earth oxides also makes possible the production of tinted glass protective windows and lenses. The formulation of glasses with lanthanum oxide content is used to prevent achromaticity in the optical lenses used, for example, in cameras for photographic reconnaissance from aircraft and satellites.

Cerium oxide-containing glass formulations can be produced to exhibit phototropic or photochromic properties. When used in eyeglasses or in goggle form these glasses can be employed to protect troops against vision harm or the flash blindness from nuclear blasts. Military personnel who wear glasses can be fitted with glare-reducing eyeglasses which adjust their transmission of light in accordance with the incident radiation so that a uniform visual field can be maintained even under low lighting conditions.

Combinations of rare earth oxides with other oxides are used to make stable inorganic pigments for yielding specific colors, e.g., yellow for use in marking the numerals and directions on vehicle instrument panels.

3. Progress in the Use of Rare Earth Oxides in Glasses

Within the glass industry of the Soviet Union there is a current awareness of the utility of rare earth oxides applied to glass technology. In commenting upon the 25th Congress of the Communist Party of the Soviet Union, Dobuzhinskii[1] stressed the important work being performed in the intensification of the glass melting process. Methods of continuous glass melting and production of articles made from crystal and colored glasses have been "invented" and placed into production. The glasses are colored with rare earth oxides and it was possible to reduce the production cycle by tenfold and to halve fuel consumption.

An example of the type of interest in colorant systems was given by Kovchur et al.[2] who desired to obtain silicate glasses possessing definite optical characteristics. They studied the effect of additives of praseodymium oxides and neodymium oxides in combination with nickelous oxide on the spectral absorption of lead-potassium silicate, low lead, and soda-lime-silica glasses. The ions of praseodymium, neodymium, and other rare earth oxides have characteristic absorption spectra in a narrow wavelength range in the visible spectrum and are suitable for coloring glasses and for obtaining different colors and shades. The rare earths caused a shift in color through transforming the yellow-colored NiO_6 complex to a violet-colored NiO_4 complex. Therefore, with only partial shifts, the praseodymium glasses ranged in color from violet, orange, pure purple, yellow, and orange-red with varying shades of intensity. Neodymia-nickel glasses were orange-yellow and purple in color. A change in the concentration of nickelous oxide in coloring glasses of different composition leads to a shift in the spectral absorption maxima and a change in the shape of the spectral absorption curves. It was found that the oxides of Pr and Nd did not form complex combinations with nickel in these glasses, with Pr and Nd existing in the form of a stable trivalent cation. These glasses found wide application in the Dzerzhinskii Borisovskii Glass Factory.

S.G. Tumanov, a long-time research worker in glass, noted that it was important to study the synthesis of pigments in the CeO_2-MoO_3 system in order to extend the range and palette of colors used in the decoration of ceramic goods and the coloring of glass.[3,4] It is known that the molybdates of rare earth elements can crystallize in two modifications: orthorhombic and tetragonal. The orthorhombic cerium molybdate is very dark, almost black in color. When, powdered, this modification appears greenish-brown. The tetragonal form of cerium molybdate is bright yellow. Mixtures of these two modifications display stable but varing color ranges. Through the use of X-ray diffraction analysis CeO_2:MoO_3 crystal rations were determined and related to the color obtained. Thus the firing of CeO_2 with excess MoO_3 in air gives rise to cerium molybdate of the tetragonal form and an intense yellow color. This pigment was found useful in obtaining a desirable pale yellow body stain, and as a glass colorant. With the addition of MgO, SrO, and BaO a yellow-green to greenish-yellow pigment could be obtained suitable for use in coloring chinaware, earthenware, and glass.

Ceria has also been found useful in a glaze composition for coating sitallized (glass-ceramic) structures for the building industry.[5] An electron microscopic study of the mechanism of opacification of CeO_2-containing lead-free glazes showed that at 800 C CeO_2 crystals begin to form, at 900 C the quantity of crystalline

phase is markedly increased, and at 1000 C with a glost firing cycle for majolica products only one crystal phase of CeO_2 appeared. The fine microstructure of the top layer of the glaze coating consists of crystallized CeO_2 and a droplet liquid structure. The reflective surface of the glazed coating is due to the partial solution and enlargement of the fused cubic crystals of CeO_2 on the surface.

As an alternative to the use of very pure raw materials to obtain optically clear glasses almost all production glass is decolorized. The most popular decolorizing agent, particularly for lead-based glasses, has been arsenic trioxide. However, arsenic trioxide is poisonous and is very difficult to store and transport. In addition, upon glass batch melting, large amounts of the arsenic are volatilized, often resulting in poor decolorizing, contamination of the plant atmosphere, and a deterioration of health conditions. It was reported by Timofeev and Aleksandriya[6] of the Krasnodarsteklotara Production Corporation that a decolorizing agent composed of rare earth oxides was developed by the Gusev Branch of the State Scientific Research Institute of Glass. The mixture comprises cerium dioxide to act as a chemical bleaching agent and neodymium and erbium oxides as physical decolorizing agents. It is important to note that although this glass factory has been in operation for decades, it was not until 1975 that rare earth decolorizing agents were introduced into the process. Such an advance was available to American industry over 35 years ago. The only inhibition to the introduction of this improvement in glass technology has been the necessity for the demonstration of the comparative economic value of rare earth decolorizers.

The synthesis and investigation of glasses for domestic glassware using rare earth oxides began on a small scale in 1960 and expanded to a broad scale usage in the next decade.[7] Rare earth compounds made it possible to exert a selection of the desired colors in glass articles. They also possess a high color purity, are solar radiation resistant, exhibit fluorescence, and show a desirable dichroism (double coloration) effect. The early glasses were melted in pot furnaces but after several years the staff of the Gusev Cut Glass Factory, the Vladimir Glass Commission, and scientists of the State Institute of Glass and its Branch at Gusev developed and introduced a continuous method of melting and working glass products colored with rare earth oxides in "sputnik" (satellite) derivatives of tank furnaces.[8] It is claimed that these furnaces were the smallest continuous glass tank furnaces developed up to the time of introduction (1965). By October 1969, The Gusev Factory[9] was able to simultaneously produce glass products of six colors and shades. In addition to the usual domestic use, the glasswares of the Gusev Factory have been widely exported to such countries as England, Canada, Denmark, Federal Republic of Germany, Syria, and Iraq.

It is worth noting that articles using rare earth oxides have increased fourfold in the last five-year plan. The Gusev Glass Factory received a "State Prize" for its work in glass for domestic and export use.

The palette of colors available from rare earth oxides, both alone or in special combinations, is great; and combined with the ancient desire of the Russian people for the possession and display of jewelry, an obvious combination is the production of colored glasses for synthetic precious stones. Some colored glasses have long been used for imitation jewelry stones. These glasses combine stability, color, brilliance, relatively high hardness, and the required high refractive

index for a good optical appearance. After a facetting production step and the application of a reflective surface layer, jewelry made from glass resembles the color and sparkle of diamonds, rubies, sapphires, topazes, emeralds, amethysts, chrysotiles, and aquamarines. It was claimed[10] that the foreign (to the Soviet Union) literature contained many compositions of colored glasses that were not of the required porperties and this necessitated the development of new glasses and colors. The Gusev Branch of the State Institute of Glass developed a continuous technological process for producing rare earth colored glasses which was put into use in the Experimental Glass Factory at Gusev. The use of some of the rare earth oxides in glass manufacture is summarized in Table 12.

Table 12. USE OF RARE EARTH OXIDES IN COLORED GLASSES

Glass Color	Colorant Composition (in kg per 100 kg of glass)	Color Tone (λ in millimicrons)
Crystal (colorless)	CeO_2-0.15, Nd_2O_3-0.0078, Er_2O_3-0.003	Decolorizing mixture
Topazes:		
Yellow	CeO_2-2.0, TiO_2-6.0	585
Orange	CeO_2-6.0, TiO_2-12.0	587
Orange	CeO_2-2.4, TiO_2-9.6, Se-0.15	610
Chrysotile:		
Light Green	CeO_2-1.5, TiO_2-4.5, $K_2Cr_2O_7$-0.06	566
Aquamarine:		
Greenish-Blue	CeO_2-1.5, TiO_2-3.0, CuO-0.16	511-517
Amethyst:		
Light Lilac	Nd_2O_3-0.5, MnO_2-0.2	441
Purple	Nd_2O_3-1.0, Er_2O_3-1.0	575
Purple	Nd_2O_3-2.5	485
Ruby:		
Rose	Er_2O_3-2.0	508
Purple	Er_2O_3-6.0	510
Purple	Er_2O_3-8.0	517

Therefore, it is concluded that the ready availability of such rare earth oxides played a part in their usage and also is a practical basis for support of the rare earth oxide production facilities.

Although CeO_2 is utilized to prevent a solarization or changes in the color of a glass due to incident radiation, the use of other rare earth oxides such as europium oxide to enable a reversible change in color of a silicate glass is well known. There are hardly any references to photochromic glass compositions in the available Soviet literature. The Soviet scientific personnel can certainly handle such work as shown by Borgman and Venger[11] who reported on the manufacture of multicolored glass articles decorated by ultraviolet irradiation of a silicate glass-containing CeO_2 and V_2O_5. The glass is initially a faint green in color as formed. After irradiation the color is transformed to a purple-violet of a highly stable nature. If an item is irradiated from only one side, a gradation of color can be obtained. The coloring effect could be reversed by heating to 400 C. The authors commented upon the potential for producing various products by this method. There is mention of research work in the synthesis of photochromic glass at the D.I. Mendeleev Institute, but no details are given.[12]

The Soviet Union produces a large number of glass items which require optical surface polishing by an abrasive. It appears that the great bulk of the abrasives are finely divided iron oxide or rouge. Due to the dirtiness of rouge polishing operations they have been eliminated in the United States. The use of the "float" glass method of flat glass manufacture became available in only a few plants in the Soviet Union within the past five years, so there would still be no real lessening of the need for abrasives. There has been an attempt to develop stabilized zirconia[13] as a softer polishing abrasive, but no further work has been reported on the subject. There appears to be very little use of ceria or rare earth oxide combinations as soft abrasives for polishing glass in the U.S.S.R. However, a more extensive search may reveal additional information.

4. Trends and Forecast

Over the past fifteen years Soviet glass manufacturers have been able to develop and use rare earth oxides, both alone and in combination, to form colored pigments and to color glass in solution color form. The processes have come from the laboratory into production use over a period of a few years, due to the location of some developmental facilities within the production unit complex. The example given here is the Gusev Glass Works with a unit of the State Scientific Research Institute located at Gusev. It is believed that the desire for export products occasioned this rare instance of easy technology transfer in the Soviet Union. Once the manufacturing process had become established the information on this subject diminished.

The use of rare earth oxides in glazes for dinnerware and for articles of construction has been noted and a continuing interest in this subject is expected.

It is believed that Soviet scientists are interested in rare earth oxide-containing glasses which exhibit photochromic properties, in rare earth oxide-modified optical glasses and special lens components, and that a continuous follow-up of current literature may reveal the extent of their interest in these subjects. Similar work in the United States is often kept in a proprietary or company confidential status so that the absence of such information should not be surprising.

In view of the necessity to upgrade working conditions it can be expected that the Soviet use of rare earth polishing compounds is already in use on a limited scale and will be extended further in time. A difficulty in changing from rouge to a cleaner abrasive is the necessity for new facilities to replace the older "dirty" facilities. Soviet managers may be reluctant to initiate such a radical step except when a new factory is to be constructed.

It is expected that the use of rare earth oxides in glasses to supply special properties as heat absorption, thermal reflectance, and radio-frequency wave protection will be of interest to Soviet scientists involved in glassmaking.

1. DOBUZHINSKII, V. I. *Towards the 25th Congress of the Communist Party of the Soviet Union.* Steklo i. Keram., v. 33, no. 1, 1976, p. 3-7.
2. KOVCHUR, S. G., SAVITSKII, S. E., SHKLYAR, Ya. V., and GAIDUK, A. P. *Effect of Rare Earth Elements in Combination with NiO on the Spectral-Absorption Properties of Glass.* Steklo i. Keram., v. 29, no. 12, 1972, p. 798-800.
3. TUMANOV, S. G., BYSTRIKOV, A. S., and PAVLOVA, V. A. *Pigments in the CeO_2-MoO_3 System.* Steklo i. Keram., v. 32, no. 7, 1975, p. 24-25.
4. TUMANOV, S. G., BYSTRIKOV, A. S., and PAVLOVA, V. A. *Influence of Alkali and Alkaline Earth Oxides Upon the Color of Pigments in the CeO_2-MoO_3 System.* Steklo i. Keram., v. 32, no. 9, 1975, p. 29-30.
5. SHTEINBERG, Yu. G., and TYURN, E. Yu. *Structure and Properties of Cerium Glazes.* Steklo i. Keram., v. 30, no. 12, 1973, p. 25-27.
6. TIMOFEEV, V. I., and ALEKSANDRIYA, V. A. *Bleaching Crystal Glasses with Acids of Rare Earth Elements.* Steklo i. Keram., v. 33, no. 1, 1976, p. 31-32.
7. YADIN, N. A. *Rare Earth Elements in the Glass Industry.* Series: Glass Industry, TsINTIL egprom, 1964.
8. FIGUROVSKII. I. A., SAVONICHEV, G. V., ZUBANOV, V. A., MOKHIN, N. F., YADIN, N. A., PCHELYAKOV, K. A., KLEGG, D. I., and SYRITSKAYA, Z. M. *Continuous Melting of Glass Stained Rare Earth Elements.* Steklo i. Keram., v. 27, no. 3, 1970, p. 131-133.
9. *The Gusev Glass Factory.* Steklo i Keram., v. 27, no. 4, 1970, p. 252-253.
10. FEDEROVA, V. A., BUGROV, A. I., CHENNYAEV, V. M., KLEGG, D. I., BLINOV, V. A., SYRITSKAYA, Z. M., and YADIN, N. A. *Development of Technological Processes for the Production of Colored Glasses Resembling Precious Stones.* Steklo i. Keram., v. 29, no. 7, 1973, p. 452-454.
11. BORGMAN, V. A., and BENGER, G. V. *The Decorative Coloring of Glassware by U.V. Radiation.* Steklo i. Keram., v. 29, no. 10, 1973, p. 655-656.
12. PAVHESHKIN, N. M. *In Commemoration of the 50th Anniversary of the D.I. Mendeleev Institute of Chemical Technology; Dept. of Glass and Pyroceramics.* Steklo i. Keram., v. 28, no. 2, 1971, p. 121-122.
13. SURKOV, M. E., KHARITONOV, F. Ya., and MASLENNIKOVA, G. N. *Stabilization of Zirconium Oxide with Neodymium Oxide.* Steklo i. Keram., v. 29, no. 1, 1972, p. 27-30.

VIII. RARE EARTH-CONTAINING PETROLEUM CATALYSTS

1. Background

In the early 1960's time frame, the greatest increase in the tonnage and total use of mixed rare earth oxides began. In fact, the largest single use ever for rare earth oxides became their content in active petroleum cracking catalysts. These special catalysts contain rare earth zeolite (molecular sieve grade) as the specific active component. From a zero initial base in 1963 there was a fantastic rate of growth until in 1970 over 90 percent of the United States fluidized bed catalytic petroleum cracking units used rare earth zeolite compounds. The content of rare earth oxides in the catalyst averages about 2.25%. In 1975 the United States consumption of mixed rare earth zeolite catalysts (assuming a 50% loss in processing) was approximately 12,000,000 pounds. Due to its pre-eminence in the field on account of its position as a source of low-cost mineral rare earths (principally bastnasite, a rare earth fluorcarbonate) from a large deposit in the low Sierra Mountains in California and the use of recently designed modern processing equipment, the Molycorp Corporation, White Plains, New York, has become the chief source of rare earth oxides for petroleum cracking catalysts. Their commanding position in this field is unlikely to be challenged before 1985.

The great significance of the use of rare earth zeolite-based petroleum catalysts is the 25% or more increase in the yield of high octane gasoline from the same crude oil feedstock. The existing catalytic cracking units utilizing the older silica-alumina catalyst formulations thereby became 25% more efficient through use of the rare earth zeolite catalysts. The result in the late 1960's was to practically halt the construction of new petroleum units because production capacity had outrun the current demand. Construction of new facilities specifically designed for the new catalysts did not resume until after 1970. It is estimated that a return to the use of non-zeolitic petroleum cracking catalysts would result in a 30 to 40% reduction in existing cracking capacity.

With the advent of the requirement for the elimination of tetraethyl lead from gasolines for new automobiles produced in the United States after 1974, newer cracking processes and better rare earth zeolite catalysts are being sought.

Rare earth-containing catalysts are also useful for promoting and allocating the direction of compound formation in both simple and complex organic systems. They can be the specific means whereby certain chemical reactions can be efficiently performed to economically produce specific organic compounds for use in reducing automotive exhaust pollution, polymerization of special plastics, and the synthesis of special hydrocarbons.

2. Military Interest

Due to the importance of gaining as great a yield of useful product from each barrel of crude oil, the type and availability of petroleum cracking catalyst is of military strategic importance. The origin, cost, and availability of gasoline, jet engine fuel, lubricants, petroleum-derived products as synthetic fibers and plastics are matters of military significance. The modern field Army cannot perform without this petroleum material base.

Specific military attention to the state of modernization of potential enemies' petroleum source, and processing should be maintained. The state of use of such rare earth catalysts give the military intelligence analysts a firm basis for presenting data for policy decisions.

The requirement for maximizing useful petroleum product yield per barrel of crude oil is a necessary adjunct to the military end-item production support base. Rare earth element-containing catalysts are consequently of prime importance to the military intelligence data base.

3. Recent Activities in the Use of Rare Earth Elements in Catalysts in the U.S.S.R.

The applications of rare earth elements in the preparation and use of rare earth-containing catalysts are widespread in the research community in the U.S.S.R. There is no concerted or centralized direction for this effort; however, there exists an intellectual as well as practical interest in these materials for performing special organic compound syntheses and in catalysts for petroleum-derived products. The research community interested in chemical catalysts and kinetics using rare earth compounds resides in the university context and falls within the realm of more or less pure research. The more pragmatic interest in rare earth compounds, especially rare earth faujasites and zeolites, is for cracking petroleum into various useful constituents. These latter applications have progressed only to the pilot-plant stage at petrochemical R&D institutes.

The most prominent Soviet individuals concerned with research-oriented rare earth element-containing catalysts are Kh.M. Minachev of the Institute of Organic Chemistry in Moscow and K.V. Topchieva of the Lomonosov Moscow State University. These authors have, with their colleagues, published a number of papers concerned with the use of catalysts to secure specific organic chemical reactions.

Some examples are indicated by Topchieva's work[1,2] on the production of isomers of hexenes and the cracking of iso-octane by zeolite type catalysts.[3] It was shown that butene isomerization and hydrogen transfer were the secondary reactions as a result of the cracking of iso-octane. The most acidic centers of the zeolite catalyst responsible for polymerization and the secondary formation of 2-butene were identical but separately positioned from those responsible for iso-octane cracking and the formation of other butenes. The direct relationship of this research work to the production of high octane fuels is noteworthy. In another paper[4] Topchieva reported on a detailed study of the mechanism of the low temperature catalysis by rare earth oxides and the reactions of H_2, O_2, C_3H_8, CO_2, and H_2O with the surface of the catalyst. The authors presented some advanced concepts correlating the nature of the active centers responsible for chemisorption and catalytic action with the scientific results of electrophysical, chemisorption, spectral, and catalytic analysis. Topchieva et al.[5] also explored the degree of hydrogenation possible in attempting to saturate simple unsaturated compounds with the use of rare earth zeolitic catalysts. United States scientists consider Mrs. Topchieva to be among the top Soviet workers in the rare earth zeolite research field.

Minachev[6] and co-workers at the Zelinskogo Institute for Organic Chemistry have performed some rather basic research on the catalytic activity of rare earth compounds and particularly upon Y-type zeolites. In the process of these hydrogenation reactions several absorbed forms of C_2H_4 and H_2 were observed as attached to the zeolites containing ion-exchanged Ba, Ca, Cu, Cr, Fe, Dy, La, or Nd and the oxides (Co_2O_3, La_2O_3, Nd_2O_3, and Dy_2O_3). The thermal desorption spectra exhibited a dependence on the nature of the ion-exchanged cation. It was observed that with increasing ion-exchanged cation content the activity of the catalyst passed through a maximum and then receded. Hydrogenation was accompanied by double-bond and skeletal isomerization. The double-bond migration occurred under milder conditions than hydrogenation. Minchav's group[7] has also used a combination noble metal-rare earth zeolite catalyst to promote chemical reactions. The introduction of one percent palladium into a CaNaY zeolite followed by heat treatment at 380 to 450 C produced a catalyst which converted C_2H_4 to C_5 and higher hydrocarbons in yields up to 83.1%; at 50 to 200 C the yields were 31.9% or less. Treatment of the catalyst with hydrogen or helium markedly reduced the catalytic activity of the zeolite compounds. Other reports by these authors are upon similar types of basic pure hydrocarbon conversion reactions utilizing rare earth oxides. Khodakov et al.[8] showed that in the isomerization of 1-butene on rare earth oxides, the catalytic activity of rare earth oxides decreased in this order: La_2O_3 greater than Nd_2O_3 which is greater than Dy_2O_3. It was reported that the LaNaY zeolite was less active catalytically than La_2O_3 (particle size less than 0.25 micron) and that the NaY zeolite was inactive. In concert with Khodakov et al., Minachev's group[9] showed that two crystalline modifications of neodymium oxide and their subsequent solution in CeO_2 and active silicates gave rise to specific catalytic activity in furthering the hydrogenation of C_2H_4. The specific catalytic activity decreased with an increase in the crystal structure coordination number of the neodymium cation. It was observed that calcination of the material to 600 C oxidized the cerium to the 4+ state. Chromium chloride and lanthanum fluoride exhibited no catalytic activity due to the screening of the cation by the instant halogen. This group has also studied[10] the effects of some rare earth cations reacted with faujasite and mordenite zeolitic forms upon catalytic reactions of acetone to form other compounds. The chief conclusions were that the rare earth cation concentration and specific lattice site positions were the most important factors controlling catalytic activity.

Some of the typical organic reactions which are made possible or improved upon through the use of rare earth cations either alone or as constituents of specially structured and specially activated complexes are shown in Table 13. The Soviet academic work is concerned with many of these types of reactions.

Some examples of this work are given by Sarmurzina et al.[11] who used intermixed precious metal-rare earth elements for reduction reactions of mesityl oxide; Slinkin and Rubinshtein[12] who reviewed the action of adsorbed and chemically reacted metal ions in zeolite structures, including comments on the ionic reduction potential and cation distribution effects. They correlated the structure of these special zeolite structures with the catalytic effects. Seleznev and Kadushing[13] reported on the existence of specific surface compounds with zeolites and made a correlation of the utility of these catalysts in promoting specific organic reaction oxidation processes. Topchieva et al.[14] has provided an excellent review of the hydrogenation reactions made possible in unsaturated organic compounds through many types of, especially rare earth reacted, zeolite catalysts.

Table 13. RARE EARTH CATALYSTS

Type of Reaction	Catalyst	Reaction
Dehydrogenation	Gd_2O_3	High Octane Gasoline
	Pt in Al_2O_3 - Pr_2O_3 CeO_2 on Zeolites	
Oxidation Reduction	CeO_2 on Al_2O_3	Oxidation of Methane
	Cu, Pr_2O_3 on Al_2O_3	Automotive exhaust gasoline oxidation
Dehydration	Y_2O_3, Dy_2O_3, Nd_2O_3 RE_2O_3	Ethyl and isopropylacohol alchols
Cracking	La_2O_3 RE-Al Silicate $CePO_4$ -Cogel	Isomerization catalyst hydrocarbons
Reforming	Cr-Al_2O_3 - RE	Nitration grade benzene from gasoline
Polymerization	Ce^{+4} salts	Vinyl polymerization on fabrics
	Pr and Y	Polymerization of acrylonitrile
Misc. Reactions	CeO_2 and Al_2O_3	Hydrocarbon synthesis
	TbO_3 on ZrO_2	Ortho hydrogen conversions
	RE carbonates (Nd, Pr)	Synthesis of Phenolic resin
	$Nd_2(Co_3)_3$ + $ErCl_3$	Preparation of polyesters

The more interesting work using rare earth catalysts for the cracking of crude petroleum and the attempt to secure the specially valuable fractions of crude oil distillates is performed away from the university oriented climate of Leningrad, Moscow, and Kiev. This work is performed in places accessible to crude oil supplies or very likely near oil-producing refinery areas as Kazakhstan, Grozny, or Ashkhabad. Ernepsov et al.[15] of the Ashkhabad Institute of Chemistry investigated the effect of specific concentration of aromatic hydrocarbon feed-stocks based upon the saturated portion of the 250 to 450 C fraction of a marine Cheleken petroleum, using aromatic contents up to 70% to be cracked with an amorphous aluminosilicate catalyst or a cerium group promoted zeolite catalyst. The cracking reaction was carried out in a vertical reactor at a temperature of 450 C and a space velocity of 1.5% per hour. At an aromatic hydrocarbon content greater than 15%, the selectivity of both catalysts decreased by about ten percent. With feeds containing aromatic hydrocarbons the rare earth zeolite catalyst exhibited a selectivity 1.2 to 1.5 times that of the commercial aluminosilicate catalyst with respect to gasoline. The gas and coke formation was also reduced by the rare earth zeolite catalyst. The yield of cracking gas also contained more saturated hydrocarbons and less hydrogen than the gas gotten from the aluminosilicate catalysts. This work is a confirmation of United States experience with such catalysts. Ernepsov et al.[16] reported high gasoline yields through cracking Cheleken off-shore petroleum fractions obtained at 350 to 450 C and a space velocity of 1.5 percent per hour. The rare earth element modified zeolite catalysts performed with much greater selectivity than other catalysts such as a commercial amorphous aluminosilicate preparation, particularly with respect to greatly improved gasoline yields from high alkane feedstocks. The rare earth catalysts were also found to markedly reduce the formation of undesirable unsaturated gas quantities.

The use of rare earth-promoted zeolite catalysts to crack petroleum fractions in an experimental refining column was reported by Sevetozarova et al.[17] An experimental rig of 65 kg per day capacity was used to study the catalytic cracking of vacuum distillates of both low sulfur (about 0.25%) high paraffinic-naphthenic (75%) and high sulfur (greater than 2%) high aromatic content (41 to 47%) petroleums. The rare earth-containing zeolite catalysts, both fresh and stabilized by an 800-hour treatment of sulfur-containing distillates, were tested at 490 C and a rate of 1.5 volumes per hour. The catalysts had a specific surface of 206 to 316 square meters per gram and a specific pore volume of 0.42 to 0.49 cc/g. Paraffinic distillates as a feedstock gave a much greater yield of gas and gasoline fractions than the aromatic distillates. The thermally stabilized catalysts yielded more butylene and isobutane than a fresh catalyst. The chief component of the C_5 fractions was isopentane, a prime gasoline ingredient. It is worth noting that the average octane value of gasoline required in the U.S.S.R. is 72; indicating that most gasoline engines used in the U.S.S.R. are of the low compression category. Despite the advent of the improved rare earth catalysts, research and development is carried on to improve conventional catalyst compositions.

In another situation, Ivanova et al.[18] of the Grozny Petroleum Institute used rare earth oxides reacted with zeolites to compare their performance with calcium aluminosilicate catalysts in the reforming of kerosene-gas oil fractions and sulfur containing 450 to 490 C fraction distillates. The catalyst was used in bead form (0.5 to 3.0 mm) in a countercurrent flow situation. The raw material flow was 0.8 to 1.5 volumes/hour and the test duration was 2000 hours. The change in catalyst activity was determined from the yield of benzene, gas, and coke. Changes in the catalyst structure were evaluated from specific surface and specific pore volume measurements. In all cases, the reduction in specific surface occurred within the first 300 to 400 hours of operation. The mean pore diameter of each catalyst increased during use. The best results were obtained with a catalyst containing about five percent rare earth oxide content. This result was attributed to the stabilizing effect of the rare earth oxide upon the zeolite aluminosilicate catalyst structure. This type of pilot-plant investigation is important for the development of the skills needed to utilize rare earth catalysts and demonstrates the current awareness of Soviet workers in the field.

Some recent patents by Soviet workers indicate their interest in rare earth-containing catalysts. Karzhev et al.[19] produced a catalyst from a combination of a Y-type zeolite with less than one percent of a noble metal such as Pd, Pt, or Re, and processing with a metal additive such as Na, Ca, Ni, Mo, and rare earth elements. The active components could range up to eight weight percent. Kaliko and his co-workers[20] produced rare earth catalysts through forming a hydrogel in a nonaqueous medium, then permitting syneresis to occur, and carrying out an ion exchange by reaction with ammonium salt solutions. The salt is washed out, then dried and calcined. To reduce the amount of rare earth compounds needed, to secure more even distribution over catalyst granules, and to prevent the decomposition of the catalyst during the final heat treatment, the rare earth cations should be incorporated into the catalyst in the hydrogel formation stage at a pH of 6.5 to 7.0. A patent by Averbukh and Pavlova[21] claims an increased activity for an aluminosilicate catalyst is promoted by a cerium phosphate (1.9 to 2.1 wt%) and P_2O_5 (0.04 to 0.06 wt%) addition reaction. This catalyst was to be used to secure the incomplete heterogeneous oxidation of methane to formaldehyde. It

is also useful for the conversion of natural gas to more valuable aliphatic organic compounds. Yermankov et al.[22] of the Institute of Catalysis at Novosibirsk have patented a variable valence rare earth catalyst for petroleum and organic reactions. Kaliko et al.[23] also patented a procedure to mold pellets from a zeolite hydrogel, and expose it to various washing treatments prior to activation with rare earth-metal salt solutions. The preparation procedures are follow-ons to the established United States procedures now widely used.

It is clear that the Soviet scientific establishment possesses the knowledge of and capacity to use rare earth catalysts in research and development and pilot reactor situations. The fact that one product Tseokar-2 has a trade name indicates that such products are becoming available. It is believed that only small quantities of rare earth zeolite catalysts are being produced, because there is no large tonnage usage for them. A list of Soviet persons active in rare earth catalyst research and development is given in Table 14.

Table 14. SOME OF THE PERSONNEL ASSOCIATED WITH THE USES OF RARE EARTH ELEMENTS IN CATALYSTS IN THE U.S.S.R.

Name	Institution	Field of Interest
A. Ya. Averbukh	Lensovet Technical Institute, Leningrad, 1974	$CePO_4$ activated alumina catalysts for heterogeneons oxidation reactions
Kh. N. Ernepsov	Institute of Chemistry of Ashkhabad, Turkomen, 1975	Ce-Group promoted zeolite for petroleum cracking
L. V. Ivanova	Grozny Petroleum Scientific Research Institute, 1974	Pilot plant study of rare earth oxides in reforming of kerosene-oil gas fractions
M. A. Kaliko		Synthesis of rare earth catalysts
Yu. S. Khodakov	Zelinskogo Institute of Organic Chemistry, Moscow, 1975	Isomerization with R.E. oxide catalysts
A. Yu. Loginov		Low temperature catalysts with rare earth oxides
Kh. M. Minachev	Zelinskogo Institute of Organic Chemistry, Moscow, 1975	Rare earth catalysts research and policy leader
I. F. Moskovskaya	Lomonosov Moscow State University, Moscow, 1975	Isomerization with rare earth catalysts
N. U. Paulova	Lensovet Technical Institute, Leningrad, 1974	Rare earth-activated alumina catalysts
V. G. Remizov		R. E. catalyst-hydrogels
A. G. Sarmurzina		Rare earth catalysts for reduction reactions
N. I. Skotnikova	Lomonosov Moscow State University, Moscow, 1975	Chemical reactions with R. E. faujasites
O. I. Svetozarova	Grozny Petroleum Scientific Research Institute, 1974	Use of R. E. Catalysts for Crude oil cracking
A. V. Topchiev	Institute of Petrochemical Synthesis, 1975	Rare earth oxide catalysts-R. E. zeolite catalysts
K. V. Topchieva	Lomonosov Moscow State University, Moscow, 1975	Rare earth zeolite catalyst, leader in U.S.S.R.
A. I. Valeeva	Grozny Petroleum Scientific Research Institute, 1974	Pilot-plant testing of rare earth zeolite catalysts
Yu. I. Yermankov	Institute of Catalysis, Novosibirsk, 1975	Rare earth catalyst research

4. Trends and Forecast

For at least a decade after the invention and application in the United States of rare earth-reacted zeolite catalysts to petroleum cracking there was no effort in the U.S.S.R. to exploit this important development. Although Soviet scientists were slow to follow this line of development, the Soviet scientists competent in catalysis in the academic area began to develop their interest several years ago and there are now a number of active academic programs which will continue due to the momentum generated by the senior scientists involved and the numbers of personnel becoming knowledgeable in this field. The academic community does not appear to intermingle with the pilot-plant institutes because of their separate interests (basic versus applied science) and their geographical separation.

Within the past few years U.S.S.R. personnel have begun to patent rare earth-containing catalyst compositions and preparation procedures. In addition, pilot-plant and small laboratory-size experimental rigs have been used to investigate the utility of these catalysts for the cracking of petroleums and feedstocks indigenous to the U.S.S.R. It is anticipated that this pilot-plant work continue for at least the next decade at the petroleum-refining institutes. It is known that some rare earth catalysts are produced for experimental use under the name of Tseokar.

There is no large-scale use of rare earth catalysts today in the U.S.S.R. because, unlike the United States and other Western nations, there is no large demand for high octane gasoline in the U.S.S.R. Table 15 is instructive in illustrating this point.

Table 15. DOMESTIC DEMAND FOR MAJOR PETROLEUM PRODUCTS, 1974
(In Barrels Per Day)

	Gasoline	Middle Distillates	Fuel Oil
U.S.A.	7,095,000	3,870,000	2,530,000
U.S.S.R.	700,000	1,400,000	4,200,000

The typical United States refinery yield per barrel of crude oil is: 48% gasoline, 28% middle distillates, 17% fuel oil, and 7% gas and coke, by volume. The refinery yield must be high for the United States as compared to the U.S.S.R. In addition, because the chief U.S.S.R. requirement is for fuel oil and the octane rating of gasoline for internal combustion engine is only 72, the needs of the U.S.S.R. are quite different from other nations. The current use of aluminosilicate catalysts can serve the needs of U.S.S.R. petroleum refiners quite well for at least the next ten years. This fact obviates the need for the U.S.S.R. to construct plants to produce rare earth-containing catalysts. It is believed that plants to make rare earth catalysts exist in the United States, Holland, and West Germany.

Information pertaining to the planning or construction of plants in the U.S.S.R. to make rare earth catalysts would be of importance. Such data would indicate whether different petroleum refinery product outputs were required to produce high octane fuel, or whether a different mix of middle distillates were needed for military fuel requirements, or whether more raw materials for the plastics or composites industry were desired. Continuous monitoring of this activity could yield knowledge as to policy and operational directions in Soviet petroleum refining, and potential consequences of Soviet strategic military decisions.

1. MOSKOVSKAYA, I. F., SINITSYNA, O. A., and TOPCHIEVA, K. V. *Isomerization of 1-Hexene on Faujasite Type Zeolites.* Zh. Fiz. Khim., v. 49, no. 10, 1975, p. 2673-2675.
2. SKOTNIKOVA, N. I., MOSKOVSKAYA, I. F., and TOPCHIEVA, K. V. *Isomerization of 2-Methyl-1-Pentene on Cationic and Cation-Decationized Forms of Zeolites.* Zh. Fiz. Khim., v. 49, no. 10, 1975, p. 2675-2676.
3. IVANOVA, T. M., ROMANOVSKII, B. V., and TOPCHIEVA, K. V. *Iso-Octane Cracking on Zeolite-Containing Catalysts: Secondary Reactions.* Vestn. Mosk. Univ. Khim., v. 16, no. 4, 1975, p. 419-423.
4. TOPCHIEVA, K. V., LOGINOV, A. Ya., and KREISBERG, V. A. *Reactions of Some Simple Molecules with the Surface of Rare Earth Oxides and the Formation of Their Catalytic Activity in Redox Reactions.* Sovrem. Probl. Fiz. Khim., v. 8, no. 4, 1975, p. 268-308.
5. TOPCHIEVA, K. V., ROSOLOSKAYA, E. N., and SHAKHNOVSKAYA, O. L. *Hydrogenation of Unsaturated Compounds on Zeolite Catalysts.* Sovrem. Probl. Fiz. Khim., v. 8, no. 3, 1975, p. 199-215.
6. MINACHEV, Kh. M., KHODAKOV, Yu. S., SAVCHENKO, B. M., and NESTOROV, V. K. *Catalytic Activity of Y-Type Zeolites in the Hydrogenation of Ethylene and Butenes.* Izv. Akad. Nauk. S.S.R. Ser. Khim., no. 8, 1975, p. 1722-1728.
7. LAPIDUS, A. L., MALTSEV, V. V., GARANIN, V. I., and MINACHEV, Kh. M. *Transformations of Ethylene in the Presence of a Palladium Y-Type Zeolite Catalyst.* Izv. Akad. Nauk. S.S.S.R. Ser. Khim., no. 12, 1975, p. 2819-2821.
8. KHODAKOV. Yu. S., NESTEROV, V. K., and MINACHEV. Kh. M. *Isomerization of 1-Butene on Rare Earth Oxides.* Izv. Akad. Nauk. S.S.S.R. Ser. Khim., no. 9, 1975, p. 2012-2014.
9. MINACHEV, Kh. M., KHODAKOV, Yu. S., MAKAROV, P. A., PANASENKO, E. B., and MASLOBOEV, V. A. *Catalytic Activity of Certain La, Nd, and Ce Compounds During Ethylene Hydrogenation.* Izv. Akad. Nauk. S.S.R. Su Khim., no. 9, 1975, p. 2015-2018.
10. MINACHEV, Kh. M., GARANIN, V. I., KHARLANOV, V. V., and KAPUSTIN, M. A. *Study of Catalytic Transformations of Acetone on Cationic Forms of Faujasite and Mordenite.* Izv. Akad. Nauk. S.S.S.R. Ser. Khim., no. 12, 1975, p. 2673-2678.
11. SARMURZINA, A. G., RAZUMKOV, A. F., and SOKOLSKII, D. V. *Mixed Rhodium Rare Earth Element Catalysts in Reduction reactions of Mesityl Oxide.* V. Sb. Prikl. i. Teor. Khimiya, Alma. Ata., v. 18, no. 6, 1975, p. 241-246.
12. SLINKIN, A. A., and RUBINSHTEIN, A. M. *Zeolite-Type Catalysts.* Prob. Kinet. Katal., v. 16, no. 2, 1975, p. 166-176.
13. SELEZNEV, V. A., and KADUSHIN, A. A. *Surface Compounds on Zeolites and Their Role in Catalytic Oxidation Processes.* Prob. Katal. Kinet., v. 16, no. 2, 1975, p. 177-178.
14. TOPCHIEVA, K. V., ROSOLOSKAYA, E. N., and SHAKHNOVOSKAYA, O. L. *The Hydrogenation of Unsaturated Compounds Upon Zeolite Catalysts.* Sovrem. Probl. Fiz. Khim., v. 8, no. 4, 1975, p. 199-215.
15. ERNEPSOV, Kh. N., SERGIENKO, S. R., DOVLETDZHANOV, A. B., and FEDEROVA, T. V. *Effect of the Concentration of Aromatic Hydrocarbons on Their Intensity and Course of Catalytic Cracking.* Ser. Fiz-Tekh. Khim. Geol. Nauk., v. 6, no. 1, 1973, p. 64-68.
16. ERNEPSOV, Kh. N., SERGIENKO, S. R., DOVLETDZHANOV, A. B., and ISHANKALIEVA, D. *Effect of Catalyst Nature and Raw Material Composition on the Degree of Catalytic Cracking.* Izv. Akad. Nauk. Turkm. S.S.R., vo. 3, no. 1, 1975, p. 33-37.
17. SVETOZAROVA, O. I., ROMANKOVA, I. K., LERASHOVA, E., NEMCHENKO, S. A., and GOLOVENKO, A. M. *Effect of Crude Petroleum Composition on the Quality of Products Obtained in Cracking with Tseokar-2 Catalyst.* Tr. Grozn. Neft. Nauchno-Issled. Inst., v. 27, no. 2, 1974, p. 23-28.
18. IVANOVA, L. V., BRESCHENKO, E. M., and REMIZOV, V. G. *Change in Properties of Zeolite-Containing Catalysts in Tests at a Pilot Plant of the Grozny Petroleum Scientific Research Institute.* Tr. Grozn. Neft. Nauchno. Issled. Inst., v. 27, no. 1, 1974, p. 103-109.
19. KARZHEV, V. I., AGAFONOV, A. V., VITUKHINA, A. S., KRUGILOV, V. Ya., KHAVKIN, V. A., GONCHAROVA, N. V., ROGOV, S. P., GELMS, I. E., and ZAITSEV, V. A. *Catalyst for Hydrogenation of Aromatic Compounds.* U.S.S.R. Patent 503, 587, 25 February 1976.
20. KALIKO, M. A., REMIZOV, V. G., RABINOVICH, S. I., BRESHCHENKO, E. M., STRIGINA, L. R., ZELTSER, Ya. I., and ATEPINA. O. G. *Rare Earth Catalysts.* U.S.S.R. Patent 392, 968, 10 August 1973.
21. AVERBUKH, A. Ya., and PAVLOVA, N. Yu. U.S.S.R. Patent 498, 030, 29 January 1974.
22. YERMANKOV, Yu. I., KUZNETSOV, B. N., DEMIN, E. A., and LAZATKIN, A. M. *Variable Valence Catalyst.* U.S.S.R. Patent 389, 828, 11 July 1973.
23. KALIKO, M. A., ZELTSTER, Ya. I., MISSIKI, Ya. V., BRESHCHENKO, E. M., REMIZOV, V. G., FILIPOV, F. I., SARYCHEVA, L. A., ARUSHANOVA, V. M., and RODITELEVA, N. M. *Zeolite Catalyst Preparation.* U.S.S.R. Patent 389, 829, 11 July 1973.

IX. NON-OXIDE RARE EARTH COMPOSITIONS

1. Background

The fact that the rare earth elements belong to the metals of the transition element groups determines not only their properties in the metallic state, but also, and more importantly, the properties of the compounds they form--in particular, compounds with the nonmetals: boron, carbon, nitrogen, silicon, and sulfur. In the formation of compounds of this type, the unfilled electron shells of these transition metals exhibit an ability to accept the valence electrons of the atoms of nonmetals. In the case of boron and silicon the result yields metallic properties, while for a case such as nitrogen the result is a more covalently bonded structure. The possibility for mixed covalent-metallic bonding which can be ascribed to these compounds influences their crystal structures and physical properties. The potentiality for wide variation in the character of the chemical bond in compounds of the rare earth metals with nonmetals supplies a significant opportunity for systematically varying the physical and mechanical properties of these compounds and producing compounds with intrinsically designed properties--electrophysical, magnetic, optical, mechanical, and refractoriness for modern technological purposes.

A significant amount of synthesis work, characterization, and analysis of these compositions was initiated and performed under the direction of Dr. G.V. Samsonov of the Institute of the Problems of Materials Management. The result was an important contribution to the basic science of rare earth compounds. References 1 and 2 are important source references for Soviet work in this area in the 1950 to the early 1960's time period.

2. Military Interest

The potential number of rare earth intermetallic compositions is quite large; however, only a few uses have been found for a very small number of these compounds. The use of lanthanum hexaboride as an electrode or channel component in magnetohydrodynamic power generation systems is experimental and may yet prove to be very important. LaB_6 may find use as a direct plug-in filament light source for external illuminating purposes. The use of rare earth borides as cathodes or coatings in miniature electron tubes would provide more stable shock-resistant units for military electronic hardware. The current usage of miniature electron tubes for military communications and control systems by the U.S.S.R. is indicative of the value of such special cathode materials. The failure of the Soviet military to develop and use solid state circuitry makes their dependence upon electron tube technology noteworthy.

The rare earth borides are also useful as electrode materials for generating electron beams and high energy beams of charged subatomic particles. For at least two decades there has been a significant Soviet effort to develop particle beam weapons. The particle beam "killer ray" concept involves the acceleration of charged particles (electrons or protons), collimating them and directing them as a continuous beam at a target by means of precisely tuned electromagnets. The analogy to a high-powered synchrotron is correct. By using such a particle beam

as a follow-on to a laser beam which can burn a hole in the atmosphere for the particle beam to ride through, vast unit energies could theoretically be emplaced upon a suitable target.

Dr. Fedorochenko of the Institute of the Problems of Materials Management has utilized a lanthanum hexaboride electrode in the design of an electron beam welding unit located at the Paton Institute. This unit was reported able to weld steel up to two inches in thickness. The advantage of performing thin-line electron beam welds upon very thick structural and armor steel components is enormous. The lack of interfering contaminating influences as well as the precision possible, coupled with preservation of initial and final steel properties is important for any military production base.

The use of rare earth sulfides, especially cerium sulfide, as a refractory or crucible material for exotic metals is well recognized. The potentiality for melting and casting uranium as well as titanium is important. The formation of sound cast structures of these metals could be made more efficient and economical through refinements in the application of rare earth sulfides.

The rare earth silicides have been reported to possess semiconductor properties (e.g., those of lanthanum and cerium) and in conjunction with their high temperature resistance and chemical stability offer a potential for the manufacture of high temperature stable circuitry as well as for semiconductor sensors for monitoring conditions within corrosive media.

3. Soviet Activity in Non-Oxide Rare Earth Compositions

After a surge in R&D activity in these materials during the 1950's and early 1960's due to Dr. Samsonov's interest, the expected wide utilization of such compositions did not occur and accordingly a lesser level of effort prevailed in the U.S.S.R. However, the utility of some of the compositions within this group gradually gave rise to a steady interest due in part to the electrical/electronic properties of these materials. Samsonov et al.[3] continued a study of the thermoemission of the rare earth borides and delineated the work function of yttrium, terbium, dysprosium, holmium, and lutetium dodecaborides. They were able to interpret the values of the work function as related to the metallic electronic structure of the compounds.

In the Ninth Scientific Conference of Graduates of the Institute of Materials Science of the Ukrainian S.S.R, Adamovskii et al.[4] noted the current interest in the preparation and investigation of the properties of compounds of the rare earth elements. There was an extensive report on the synthesis of erbium, holmium, ytterbium, and lutetium sesquiselenides. Work was being carried on upon the ultraviolet and infrared absorption spectra of thin films of lanthanum sulfide corresponding to formulas in the stoichiometric form of Me_2X_2. The relationship between the transmission coefficient and the energy of photons and mechanism of electron transitions in lanthanum sesquisulfide was determined. The requirements for thermoelectric materials based upon rare earth elements and refractory compounds of the transition metals were also formulated at the Institute. The influence exerted by the character of band overlap on the thermoelectric value coefficient was investigated. The thermionic emission properties of bulk specimens of lanthanum hexaboride alone and in combination with 50 mole percent of the

refractory compounds (TiC, NbC, WC, and TiB_2) and nickel was studied. A study was also made of the electrophysical properties of films of various rare earth hexaborides deposited by the electron beam evaporation technique. The current Institute work appears to be primarily of a fundamental rather than an applied nature.

The co-sintering of yttrium boride and lanthanum hexaboride has been reported by Shlyuko et al.[5] of the Kiev Polytechnical Institute who reported enhanced densification and the variable physical properties of these compositions. The thermoemissive properties of some specimens were very good.

Grizik[6] reported the preparation of rare earth and yttrium sulfides by means of a thiocyanate process. There were no property measurements reported on the stability of the materials. However, the process synthesis was novel. Europium sulfide films resistant to oxidation were reported by Palatnik.[7]

Spiridinov[8] of the Institute of High Temperatures has reported the preparation of rare earth oxyfluorides and has investigated lanthanum sulfide (La_2S_2) and cerium sulfide (Ce_2S_2) for use as high temperature thermoelectrics for broad band conductors. Lugin et al.[9] of IHT have also investigated rare earth nitrides as potentially useful thermoelectric materials. Some of the Soviet personalities associated with work on non-oxide rare earth compositions are listed in Table 16.

Table 16. SOVIET PERSONNEL ASSOCIATED WITH NON-OXIDE RARE EARTH COMPOSITIONS

Name	Institution	Field of Interest
V. P. Bondarenko	Institute of High Temperature, Moscow, 1975	Rare earth borides
E. I. Gladyshevskii		Rare earth silicides
M. S. Kovalchenko	Institute of Problems of Materials Management, Kiev, 1975	Rare earth borides
V. V. Morozov	Kiev Polytechnical Institute, Kiev, 1975	Additives for Improving Densification of LaB_6
V. S. Neshpor	Institute of Problems of Materials Management, Kiev, 1976	Properties of rare earth intermetallic compounds; thermal & electrical conductivity, LaB_6
Yu. B. Paderno	Institute of High Temperatures, Moscow, 1975	Rare earth intermetallic (MHD)
G. V. Samsonov (deceased 1975)	Institute of Problems of Materials Management, Kiev	Rare earth borides, nitrides carbides, silicides synthesis, properties & uses. Pioneer and leader of rare earth R&D
V. Ya. Shlyuko	Kiev Polytechnical Institute, Kiev, 1974	Sintering of lanthanum boride
E. I. Taldaev		Vapor deposition of CeF_3-optical coating

There have been no worthwhile references available on the rare earth carbides in the past few years due to the fact that, as Samsonov[1] stated in 1964, there have been no uses found for the carbides of the rare earth elements.

The only really new use of a non-oxide rare earth material during the past few years was the invention reported by Taldaev[10] of a thermally stable coating on an unidentified optical ceramic known as KO-2. A coating system was claimed

based upon zinc sulfide and SrFe layers with the final surface layer composed of cerium fluoride. The advantage gained was a thermally stable coating and increased radiation transmission in the 7 to 12 micron range.

It is concluded that the activity in rare earth non-oxide compositions is relatively small and chiefly performed at institutes in Moscow and Kiev.

4. Trends and Forecast

For over a decade, spurred on by the intense interest of G.V. Samsonov in the late 1950's and early 1960's, the non-oxide rare earth compositions were the subjects of preparation, characterization, and property measurement activity. However, as Dr. Samsonov's interests became more general due to his assumption of broader administrative and scientific activities, the interest in this highly specialized area waned. From 1970 to the present only minor interest in these compositions is apparent.

It appears that unless some of these materials show specific promise for a particular application either for military use or for some industrial purpose, only small amounts of basic research on non-oxide rare earth compositions will be performed in the Soviet Union. There seems to be only faint although continuing interest in these compositions at the Institute of High Temperatures and the Institute of Rare Metals in Moscow and at the Institute of the Problems of Materials Science at Kiev.

1. SAMSONOV, G. V. *High Temperature Compounds of Rare Earth Metals With Nonmetals.* Metallurgiya, Moscow, 1964.
2. ZELIKMAN, A. N., KREIN, O. E., and SAMSONOV, G. V. *Metallurgy of Rare Earth Metals.* Izdatelstvo Metallurgiya, Moscow, 1964, p. 467.
3. SAMSONOV, G. V., OKHREMCHUK, L. N., PODCHERNYAEVA, I. A., FOMENKO, V. S., and ODINTSOV, V. V. *Thermoemission of Rare Earth Dodecaborides.* Simp. Boru., v. 4, no. 1, 1974, p. 245-247.
4. ADAMOVSKII, A. A., VYALTSEV, A. M., and LUCHKA, M. V. *Ninth Conference of the Institute of Materials Science, Academy of Sciences. Ukrainian S.S.R.* Poroshkovaya Metallurgiya, v. 153, no. 9, 1975, p. 101-106.
5. SHLYUKO, V. Ya., MOROZOV, V. V., BESOV, A. V., CHERNYAK, L. V., and GUZENKO, L. V. *Effect of Additives of Yttrium on the Sintering and Properties of Lanthanum Hexaboride.* Prosh. Met., v. 152, no. 7, 1974, p. 29-33.
6. GRIZIK, A. A., and BORDUKENKO, G. P. *Preparation of Rare Earth and Yttrium Sulfides by a Thiocynate Process.* Tsvetn. Met., no. 1, 1975, p. 47-48.
7. PALATNIK, L. S., MARINCHEVA, V. E., and MABOKA, M. N. *Structure of Oxidized Europium Sulfide Films.* Neorg. Mater., v. 11, no. 5, 1975, p. 814-818.
8. SPIRIDINOV, F. M. *Properties and Preparation of Some Rare Earth Oxysulfides.* Zh. Fiz. Khim., v. 49, no. 5, 1975, p. 1340-1344.
9. LUGIN, L. G., TYURIN, Y., and CHUKALIN, S. *Some Properties of Rare Earth Nitrides* in Research Results at the Institute of High Temperatures, 1971, p. 6-7, Nauka Press, Moscow, 1972.
10. TALDAEV, E. T. *Low Reflective Optical Coating.* U.S.S.R. Patent 449, 893, November 15, 1974.

X. ELECTRIC/ELECTRONIC RARE EARTH MATERIALS

1. Background

The unfilled inner electron shells of the rare earth elements give rise to certain electric and electronic properties which make the rare earth-containing compounds valuable for many purposes. The uses to which such materials have been put includes heating elements for high temperature furnaces, inorganic thick-film resistors, temperature-stable capacitors, luminescent compounds, phosphors, thin-film substrates, piezoelectric materials, electro-optic materials, semi-conductors, and magnetic bubble-containing microstructures for computer memory components. From laser ion compounds to substrates to microwave uses the rare earth elements have found a use in almost every field of electric and electronic use.

2. Military Interest

The modern Army has become attuned to the necessity for utilizing both simple as well as sophisticated means for both initiating and controlling firepower. Communications and guidance systems have become necessary and commonplace both in defensive as well as battlefield areas. Even the production support base has become dependent upon electrical and electronic materials and these often utilize rare earth elements as essential constituents.

The electronic black boxes containing myriads of components use rare earths in temperature-compensating capacitors, thick-film resistors, microwave tuning devices, and frequency-switching circuitry. Such commonplace items as instrument panel illuminators also use rare earths in the form of phosphors.

Developmental military electronic items as fuel cells, thermoelectric generating devices with a solid electrolyte, large-scale integrated circuits, temperature sensing devices for jet engines operating at very high temperatures, surface-protective infrared transmitting films for coating the optics of infrared seeking devices, fiber optic control devices, and microcomputer components, all utilize rare earth compounds in some form. The pervasive use of rare earths in a multiplicity of types and forms both as major and minor constituents is a significant feature in the modern technological support base for military end items.

3. Utilization of Rare Earths in Soviet Electric/Electronic Technology

The primary consumer of electric/electronic hardware in the Soviet Union is the military establishment. The widespread dissemination of electric/electronic end items is unknown in the Soviet Union. Solid state electronics and computer technology are not in use by the vast bulk of the Soviet civilian industrial sector. In fact, in Soviet research and development laboratories the presence of Western electronic hardware is considered a sign of high status due to the import controls exercised by the U.S.S.R. Only if a project is considered sufficiently valuable or if the prestige of a particular scientist is politically adequate can the necessary import controls be relaxed. In general, it can be said that the conceptual base for electric/electronic development postdates the Western establishment by from 5 to 15 years. There exists a broad range of activity in the electric/electronic area and some examples will be presented to indicate the extent of current Soviet work in these areas.

As an example of the lag in Soviet technology, consider the field of rare earth phosphors. In the United States the maximum activity in this area began in the late 1950's and lasted for about five to eight years, whereas the same rare earth compositional field is now being systematically investigated in the U.S.S.R. Kaplan et al.[1] recently patented a grouping of yttrium oxysulfide, terbium oxyvanadate, samarium, and yttrium oxysulfide combination phosphors. Borisov et al.[2] also patented a group of europium-activated tantalum oxide phosphors. Soshchin[3] reported on the comparative efficiencies of the activated luminescence of gadolinium oxysulfide and gadolinium terbium oxysulfide for use in the detection and amplification portions of X-ray screening devices. Panchenko[4] has patented a yttrium-cerium silicate phosphor which shows increased life stability over similar cerium-activated compounds. Soshchin[5] recently patented a terbium-activated yttrium gadolinium or lanthanum oxysulfide luminophase. The classic example of research lag is the report by Krongauz[6] of europium-activated phosphors. These same compounds were active subjects for research in the United States as long ago as 1956 and were commercialized in 1962. An indication of the possible preparation for color television tube phosphors within the U.S.S.R. is a patent for a blue phosphor based upon Ce-Y-silicate invented by Morozova and Rumyantseva.[7] The reduced voltage requirements for activation fit in well for the lesser requirements that high voltage device designers desire for simplicity and reduced cost of manufacture.

There is a continuing interest in materials for use as the electrodes in arc, pulsed, and high intensity light sources. Faifer et al.[8] reported on the use of samarium oxide to improve the emission and life characteristics of tungsten electrodes. Kulvarskaya[9] investigated the thermionic emission from a number of rare earth oxide cathodes with particular emphasis on yttrium oxide. He noted the suitability of these materials for the purpose and commented upon cathode design factors, emphasizing the need for high-purity rare earth oxides in order to separate out unwanted variables. Busol[10] reported an improved material for electrodes for pulsed sources of high intensity light. This yttrium oxide tungsten material provided a potential high energy source for pulsing lasers with increased efficiency. The potential application for weaponry is clear. The rare earths are also used in the cathodes of high pressure lamps. Emelyanov et al.[11] used dysprosium oxide, holmium oxide, and terbium oxide as essential ingredients in high pressure lamp cathodes. Korochkov et al.[12] patented a high pressure gas discharge lamp using an yttrium oxide additive to secure longer life and better color balance.

There has been an attempt from time to time on the part of Soviet technologists to prepare oxidation-resistant heating elements for industrial furnace use and for the generalized resistance heater field. Alekseenko et al.[13] determined the electrical resistance/thermal properties of yttria-containing calcium-stabilized zirconia and noted the promise of the material for resistance heating and for MHD purposes. Gorbunora and Strakhov et al.[14] at the Lensovet Technical Institute in Leningrad patented a resistance heater element composed of a rare earth chromite 45 to 90 parts by weight and 1 to 55 parts of an alkaline earth zirconate. They claimed the element could be started up at room temperature and could operate in air at temperatures up to 1750 C. The composition is thought to contain lanthanum chromite as the specific rare earth compound used in the formulation.

The use of rare earths for thick-film resistors was reported by Bazhev et al.[15] They investigated the compositional limits for these compounds which are analogous to the tungsten bronzes in crystal structure and electrical behavior. Thick-film capacitor elements utilizing lanthanum oxide as a constituent have been reported by Mudrolyubova et al.[16] They used combinations of nickel powder, chromium oxide, lanthanum oxide, and titanium oxide to form various capacitor compositions. Chistyakov and Zaichkin[17] reported on the structure and properties of cerium oxide, neodymium oxide, dysprosium oxide, holmium oxide, and combinations thereof as suitable thin-film dielectric capacitors. The films were prepared by vapor deposition and possessed good durability. Chernobrovkin[18] described holmium oxide, yttrium oxide, dysprosium oxide, and lanthanum oxide as suitable vapor-deposited thin-film capacitor elements. These activities indicate that a research background in solid state circuitry is being developed at Soviet institutes. High frequency ceramic capacitors have been patented by Aksenova et al.[19] who described a lanthanum oxide-containing ceramic capacitor composition. The combination of a barium oxide-aluminous clay with lanthanum oxide, when carefully heat treated, yielded a successful high frequency voltage resistant fully inorganic capacitor body. The application of rare earth to aircraft electronic circuits is demonstrated by a patent by Chernobrovskii[20] of the Kuibashev Aviation Institute on a dielectric material composed of holmium oxide, 10-20 wt%; Dy_2O_3, 10-20 wt%; and Y_2O_3 the balance. This material is used in thin-film condensers for integrated circuits. The electrical strength is given as 3 to 8 x 10 volts/cm. These films are prepared by vacuum evaporation. Aluminum films were evaporated onto the rare earth oxides to serve as the condenser containers.

The utilization of rare earths in a thermoelectric device is illustrated by the work of Tananaev et al.[21] who added 1 to 20% of powdered borates of the general formula $Ln_2M_3(BO_3)$ where Ln = rare earth metal, M = alkaline earth metal. The addition of this material to graphite electrodes yielded vastly improved oxidation resistance at a cathode operating temperature of 1400 C. For fuel cell technology there is a continuing interest in rare earth-stabilized zirconia as a solid electrolyte. One example of this type of work is the report by Tokovoi et al.[22] on the properties of zirconia stabilized with calcium oxide, yttrium oxide, and scadium oxide. The thermal/electric stability of these compositions was reported as excellent. Tikhonov et al.[23] also reported on the synthesis, the thermal stability, and high temperature electrical properties of zirconia stabilized with a calcium oxide-yttrium oxide combination. The work in different phases on zirconia stabilized with mixed rare earths for solid electrolytes for fuel cells indicates that this material class has been chosen as the most suitable material for advanced fuel cell development in the U.S.S.R. Specific details of the oxygen permeability of rare earth-zirconia solid electrolytes were given by Polguev et al.[24] who used structures of 90.0% mole% (m/o) ZrO_2 plus 10.0 m/o Y_2O_3; 89.0 m/o ZrO_2 plus 8 m/o Y_2O_3 plus 3.0 m/o Al_2O_3; and 90 m/o ZrO_2 plus 10.0 m/o Sc_2O_3. The oxygen permeability in a range of oxygen partial pressures of 0.01 to 1.0 atmosphere for the temperature range of 900 to 1250 C was found to be proportional to $P_{O_2}{}^{1/4}$. They showed that the diffusion coefficient of oxygen does not depend upon its pressure in a gas atmosphere.

An apparent center for research activities on piezoelectric ceramic materials is located at Rostov State University. A recent patent[25] on a high temperature stable piezoelectric material composed of Bi_2O_3-78 wt%, TiO_2-20 wt%, Nd_2O_3-1 wt%,

and Nb_2O_5-1 wt% had a Curie point of 643 C and exhibited almost no change in d_{33} over the 20 to 400 C temperature range and the 10 to 3000 kg/cm^2 pressure range. The leader of this group is Dr. Vusevkev. The assignment of the patent to the Rostov State University is noteworthy as it gives this educational institution control over its use in the U.S.S.R.

The rare earths have also found use in electro-optical effect materials. An expert in this field is Anistratov[26] who has written extensively on the variation of the optical properties of materials during phase transitions. He reviewed the changes in electro-optical, photoelastic, and other effects during ferroelectric, improper ferroelectric, and structural transitions. He did not treat the lead lanthanum zirconate materials discovered in the U.S. some years ago. Typical of many papers in the literature is that by Klimov et al.[27] who reported on the electro-optical and piezo-optical hysteresis of both pure and Nd^{3+} activated (0.5%) Gd_2MoO_4. The piezo-optical coefficients of the doped material were 30% larger than those of the pure material. The spontaneous polarization and the induced electro-optical coefficients were in good agreement with theoretical model predictions. An example of the complexity of rare earth usage is shown in the magneto-optical studies of the magnetic phase diagram of $[(Gd, Tb, Er)_3(Al, Fe)_5O_{12}]$ reported by Balyaeva[28] of the Low Temperature Institute at Kharkov. $Gd_{0.98}Tb_{0.69}Er_{1.33}Al_{0.15}Fe_{4.85}O_{12}$ single crystals were prepared and the phase diagram at H = 0 to 40 Oersteds was determined at 4.2 K.

A significant amount of work is being performed on metal oxide semiconductor devices in the U.S.S.R. Rozhkov et al.[29] reported on the usage of Y_2O_3 and La_2O_3 films in MOS structures. Chernobrovkin[30] described the current voltage characteristics of terbium oxide insulating layers in an MOS type structure. The terbium oxide layer exhibited negative voltage characteristics. Novichkov et al.[31] commented on the electrophysical properties of MOS structures containing N-gallium arsenide-erbium oxide-aluminum and N-gallium arsenide-dysprosium oxide-aluminum. Resistivities, capacitance voltage, and dielectric properties were examined and reported.

The use of rare earth compounds in electric and electronic technology is sufficiently widespread as to make this brief survey only an indication of the extent to which research and development activities in rare earths for such uses are carried on the U.S.S.R. There are literally hundreds of potential applications of the rare earth elements as constituents of materials which are used in electric/electronic devices. The field is so extensive a separate study could be devoted to it. Therefore this section can only be considered as indicative of such activity and can only serve as a guide for additional study. Some of the Soviet personnel associated with work upon rare earth materials for electric/electronic applications are presented in Table 17.

4. Trends and Forecast

Although there appears to be a significant body of R&D work on rare earth usage in the Soviet Union, the industrial utilization of end items based upon this work seems to be rather low. In general, it appears that for most areas there is a 5 to 15-year time lag in the utilization of rare earth-based electric/electronic technology within the U.S.S.R. From phosphors to MOS circuits to computer devices

Table 17. SOVIET PERSONNEL ASSOCIATED WITH ELECTRIC/ELECTRONIC RARE EARTH MATERIALS

Name	Institution	Field of Interest
A. M. Balbashov	Moscow Energy Institute, Moscow, 1976	Thermo-Magnetic Recording Devices, Epitaxial Films
A. Ya. Chervonenkis	Moscow Energy Institute, Moscow, 1976	Rare Earth Containing Electronic Substrates
V. A. Dubok	Institute of Problems of Materials Management, Kiev, 1976	Solid Electrolytes, Electrical Insulators
E. K. Keler	Grebenshchikov Institute of Silicate Chemistry, Leningrad, 1975	ZrO_2-Y_2O_3-CaO-Fuel Cell Solid Electrolyte
I. M. Klimov	Lvov State University, Lvov, 1975	Piezo-Optical, Electro-Optical Ceramic
B. S. Kulvarskaya	Institute of Radiotechnology & Electronics, Moscow, 1976	Electron Tube Cathodes, Light Source Electrodes
V. V. Lashneva	Institute of Problems of Materials Management, Kiev, 1976	Solid Electrolytes, Electrical Insulators
S. F. Palguev	Institute of Electrochemistry, Ural Scientific Center, Sverdlovsk, 1975	Fuel Cell-Solid ZrO_2 Electrolytes
V. A. Rozhkov		Metal Oxide-Semi Conductor Technology
P. H. Tikhonov	Grebenshchikov Institute of Silicate Chemistry, Leningrad, 1975	ZrO_2-Y_2O_3 Fuel Cell Solid Electrolyte
Yu. A. Vuseokev	Rostov State University, Rostov, 1975	Piezoelectric Materials

the Soviet research and development effort follows that of the United States. The lag is particularly long for consumer-related items. The electronic base for communications and guidance has concentrated on miniature electron tube technology rather than the all solid-state applications pioneered in the United States and Japan. It appears that the lack of an electronic-consumer base has hampered military electronic developments in the U.S.S.R.

Although there is a strong research interest in MOS technology it is believed that the Soviet Union will attempt to purchase rather than develop the technology to mass-produce MOS devices. By delay they can purchase the latest MOS technology and leapfrog the interim developmental stages. The latest and most advanced MOS memory chip circuit for computers with access time in the 45-nanosecond range has 4,096 memory cells with a 4-micron gate size. It is believed that it would take at least ten or more years for the U.S.S.R. to develop a similar technology in this sophisticated, highly specialized field.

The absence of work on PLZT materials either indicates that all such work is covered by military secrecy or more likely it will take another year or two before some Soviet scientist undertakes an interest in this type of material of high potential military value.

It would appear to this analyst that the more advanced electronic technology utilizing rare earth compounds would be developed exclusively for military purposes resulting in the lack of substantial material on the subject in the available literature. It would also account for the relative lack of data on rare earth electric/electronic manufacturing technology in the available literature. The scarcity of such material is likely to continue into the indefinite future as it is unlikely that the Soviet Union will sell or commit its most advanced electronic hardware to exposure to Western nations.

1. KAPLAN, G. E., BOEV, E. I., MONASHIROV, O. Ya., POSTOLOVA, L. M., MOISEEV, S. D., ANUFRIEV, I. I., MIKHALEV, A. A., and MIRONENKO, V. M. *Rare earth Oxysulfide Phosphors.* U.S.S.R. Patent 442, 697, 1975.
2. BORISOV, A. K., KRYLOV, E. I., SHULGIN, B. V., and KAZANTSEV, V. V. *Luminescent Composition Based on Tantalum Oxides Using Europium as an Activator.* U.S.S.R. Patent 403, 316, 1974.
3. SOSHCHIN, N. P. *Comparative Efficiencies of the Luminescence of Gadolinium Oxide and Gadolinium Terbium Oxysulfide.* Lyumin. Rentgenovskago Izluch., v. 32, no. I, 1974, p. 34-37.
4. PANCHENKO, T. A., BOEV, E. I., and SOGR, T. V. *Cerium Activated Yttrium Silicate Phosphor.* U.S.S.R. Patent 479, 978, 1976.
5. SOSHCHIN, N. P., and AMIRYAN, A. M. *Terbium Activated Phosphors.* U.S.S.R. Patent 477, 184, 1976.
6. KRONGAUZ, V. G., and KAPLENOV, V. G. *Photo and Thermostimulation of Luminescence of Europium Activated Yttrium Oxide.* St. Nauchn. Tr. Vses. Inst. Lyuminoforov Osobo. Chist. Veshchestv., v. 9, no. 2, 1973, p. 112-115.
7. MOROZOVA, A. V., and RUMYANTSEVA, T. Ya. *Blue Phosphor Activated With Cerium.* U.S.S.R. Patent 405, 384.
8. FAIFER, S. I., MOROKOV, V. I., SAVRANSKAYA, E. S., IONOV, V. I., DIGOEV, A. K., KUZNETSOV, P. F., and KOROKII, A. I. *Material for the Electrodes of Arc and Pulse Light Sources.* U.S.S.R. Patent 444, 269.
9. KULVARSKAYA, B. S. *Analysis of Factors Concerning the Thermionic Emission of Cathodes of Rare Earth Oxides.* Zh. Tekh. Fiz., v. 46, no. 7, 1976, p. 1501-1504.
10. BUSOL, F. I., MOROKOV, V. I., FAIFER, S. I., MEERSON, G. A., KOZLOV, N. A., and TUMANOV, A. N. *Yttrium Oxide Tungsten Electrode.* U.S.S.R. Patent 513, 410.
11. EMELYANOV, N. I., KOROCHKOV, Yu. A., and RUDENEV, V. N. *Use of Rare Earth Oxides in the Cathodes of High Pressure Lamps.* Svetotechnika, no. 1, 1973, p. 14-15.
12. KOROCHKOV, Yu. A., PRESTOVIT, V. M., and LAVRENTEV, B. V. *High Pressure Lamp.* U.S.S.R. Patent 485, 513.
13. ALEKSEENKO, L. S., KOIFMAN, G. Yu., POSOKHOVA, E. D., and SHAKHBIN, D. M. *Electrical Resistance of Stabilized Zirconium Dioxide at Elevated Temperatures.* Neorg. Mater., v. 10, no. 11, 1974, p. 2006-2008.
14. GORBUNOVA, K. N., and STRAKHOV, V. I. *Rare Earth Chromite Refractory Heating Element.* U.S.S.R. Patent 499, 248, 1976.
15. BAZHEV, G. V., MAKAROVA, D. V., and SHVEIKIN, G. P. *Europium-Niobium Oxide Bronzes.* Dokl. Akad. Nauk. S.S.R., v. 223, no. Z, 1975, p. 358-361.
16. MUDROLYUBOVA, L. P., ROTENBERG, B. A., LIMAR, T. F., and CHEREDNICHENKO, I. F. *Ceramic Capacitor.* U.S.S.R. Patent 474, 861.
17. CHISTYAKOV, Yu. D., and ZAICHKIN, N. N. *Structure and Properties of Rare Earth Metal Oxide Films.* Mikroelektronika, v. 4, no. 2, 1975, p. 157-160.
18. CHERNOBROVKIN, D. I. *Dielectric Material for Thin Film Elements.* U.S.S.R. Patent 470, 872, July 19, 1973.
19. AKSENOVA, L. A., MUDROLYUBOVA, L. P., and ROTENBERG, B. A., U.S.S.R. Patent 478, 813.
20. CHERNOBROVSKII, D. I. *Rare Earth Condensers.* U.S.S.R. Patent 470, 872.
21. TANANAEV, I. V., DZURRIASKII, E. F., and KULVARSKAYA, B. S. *Improvement of Thermoelectric Cathode.* U.S.S.R. Patent 498, 659.
22. TOKOVOI, O. K., POVOLOTSKII, D. Ya., ZOLOTAREVSKII, B. M., ALEKSEENKO, E. S., and GOVALEV, S. N. *Study of the Properties of a Solid Electrolyte of ZrO_2 Stabilized Wtih CaO, Yttrium Oxide, and Scandium Oxide.* Tr. Chelyab. Politekh. Inst., v. 33, no. 1, 1975, p. 64-67.
23. TIKHONOV, P. A., KUZNETSOV, A. K., KELER, E. K., and KRAVCHINSKAYA, M. V. Neorg. Mater., v. 11, no. 4, 1975, p. 690-694.
24. POLGUEV, S. F., GILDERMAN, V. K., and NEUIMIN, A. D. *Permeability of Stabilized Zirconia Solid Electrolytes.* J. Electrochem., Soc., v. 122, no. 6, 1975, p. 745-748.
25. VUSEVKEV, Yu. A., EPREMYAN, L. G., and GURVICH, Y. V. *Temperature Stable Piezoelectric Ceramic Material.* U.S.S.R. Patent 497, 267, 1975.
26. ANISTRATOV, A. T. *Transformation of Optical Properties of Crystalline Dielectrics During Phase Transitions.* In Fazouye Perekhody Krist., Siberian Akad. Nauk., 1975, p. 150-206.
27. KLIMOV, I. M., and BLOKH, O. G. *Spontaneous Birefringence in Gadolinium Molybdate.* Izv. Akad. Nauk. S.S.S.R. Ser. Fiz., v. 39, no. 5, 1975, p. 978-982.
28. BALYAEVA, A. I., VAISNORAS, R., PETROVA, G. P., POTAKOVA, V. A., SILAEV, V. I., and STEL'MAKHOV, Yu. N. *Spectral and Magnetooptical Studies of the Magnetic Phase Diagram of a Rare Earth Garnet Composition at Low Temperatures.* Fiz. Nizk. Temp. (Kiev), v. 1, no. 8, 1975, p. 1001-1006.
29. ROZHKOV, V. A., VDORIN, O. S., KOTELOV, V. N., and SVERDLOVA, A. M. *Metal Oxide Semi-Conductor Structures. Containing Rare Earth Films.* Poluch. Svoista, Tonkikh Plenok, no. 1, 1973, p. 3-12.
30. CHERNOBROVKIN, D. I. *Thin Film-Dielectric-Metal Structure with N-Type Characteristics.* Mikroelektronika, v. 3, no. 5, 1974, p. 461-462.
31. NOVICHKOV, V. V., SVERLOVA, A. M., NOVICHKOVA, N. P., and ROZHKOV, V. A. *Electrophysical Properties of MOS Devices.* Mikroelektronika, v. 5, no. 1, 1976, p. 24-27.

XI. CONCLUSIONS

It is concluded that the basis for the significant and extensive research, development, and applications of the rare earth element ceramic compounds and compositions within the Soviet Union is not the result of a centrally directed activity for some highly specialized strategic effort. Rather this sophisticated activity is attributable to the fundamental worth of these highly specialized materials for providing particularly valuable properties in a wide variety of useful fields of the industrial and military endeavor within the U.S.S.R.

Advanced military weapons systems such as laser weapons, magneto-hydrodynamic power generation sources, electronic circuitry for computer-assisted guidance and fire control, early warning high power radar systems, precision-guided missiles, proximity-fuzed devices, and many other end items all utilize the rare earth elements in some form as essential components. The military production support base also requires the use of rare earth elements in many forms ranging from chemical reaction promoters to electric power generation and distribution, as well as for petroleum cracking catalysts. The acquisition of current data from open source literature can yield reliable and valuable data on research and development activities as well as for future applications of rare earth element compositions for military and industrial uses in the U.S.S.R.

It is concluded that the updating of open source data on rare earth compound availability and usage on a timely basis can supply scientific intelligence analysts with the advance indicators required to form highly reliable predictions as to the state of and potential time of deployment of advanced weapons systems. The infusion of this knowledge of activities within the U.S.S.R. into the United States decision-making process data base is a means of helping to provide for an adequate response to another nation's military capabilities.

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RARE EARTH CERAMIC TECHNOLOGY (U.S.S.R) -
Morton I. Kliman

Technical Report AMMRC TR 78-3, January 1978, 79 pp -
illus-tables, FSTC Project 4217154,
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Key Words

Rare earth elements
Magnetohydrodynamic generators
Ferroelectric materials

This study presents and documents an analysis of the sources and uses of rare earth element oxides and ceramics in the *Union of Soviet Socialist Republics. The* purpose of this study is to provide an adequate basis for the comprehension of the strategic background for the uses of rare earth compounds. With this knowledge the addition of new information can be properly applied to understand the level of technology and rate of advancement of rare earth compound technology within the U.S.S.R. as well as other nations. This data base is intended to provide further support for the acquisition and placement of new data into proper prespective for rapid, up-to-data technological assessments. The information contained in this study is based upon open source scientific and technical literature.

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